QUINODIMETHANE AND NAPHTHOQUINODIMETHANE COMPLEXES OF RUTHENIUM (0)

a thesis presented

by

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to the

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in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews June 1989

DECLARATION

I Nigel John Simpson hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed . Date 30th June 1989

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on 1st Oct 1985 and as a candidate for the degree of Ph.D. on 1st Oct 1986.

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I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the degree of Ph.D.

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TO

MUM and DAD

Oh who can tell, save he whose heart hath tried,
And danced in triumph o'er the waters wide,
The exulting sense - the pulse's maddening play,
That thrills the wanderer of that trackless way?

Lord George Byron

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LIST OF ABBREVIATIONS

Chemical	
PPh_2Me	methyldiphenylphosphine
PMe_2Ph	dimethylphenylphosphine
PEt_3	triethylphosphine
PMe_3	trimethylphosphine
TMEDA	tetramethylethylenediamine
$P(OPh_3)_3$	triphenylphosphite
C_5H_5 , Cp	cyclopentadienyl
COD	cyclo-octa-1,5-diene
$P(OMe)_3$	trimethylphosphite
t-BuOK	potassium tert-butoxide
C_6Me_6	hexamethylbenzene
dmpm	bis(dimethylphosphino)methane
dmpe	bis(dimethylphosphino)ethane
C_5Me_5	pentamethylcyclopentadienyl
PPh_3	triphenylphosphine
BuLi	butyllithium

N.M.R

s	singlet
d	doublet
t	triplet
q	quartet
qu	quintet
m	multiplet
b	broad
p	pseudo
a	apparent

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ABSTRACT

It has previously been shown that reactions of [$RuCl_2P_4$] , (P = PPh_2Me , PMe_2Ph or PEt_3) , with o-$MeC_6H_4CH_2MgBr$ produce compounds analyzing as [$Ru(CH_2C_6H_4CH_2)P_3$] ; complexes which contain an o-xylidene ligand.
The reaction can be developed and extended by the use of organolithium reagents , as an alternative to the Grignard reagents.

Reactions of [$RuCl_2P_4$] , (P = PPh_2Me or PMe_3) , with the lithium salts of o-xylene , 1,2,4,5 - tetramethylbenzene , 1,2,3 - trimethylbenzene and 1,2,3,4 - tetramethylbenzene yield complexes which can be described as containing o-xylidene and methyl substituted o-xylidene ligands.

A spectroscopic examination of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] by ^1H n.m.r , ^{31}P n.m.r and ^{13}C n.m.r , coupled with the techniques of Resolution Enhancement , 2-D n.m.r and Coherent Wave Decoupling allows complete characterization of the compound which can be said to to contain an intermediate σ^2,π - π^2 metal - xylidene interaction. The o-xylidene ligand in these complexes can thus be more specifically termed as a quinodimethane ligand.

Reaction of 1-lithiomethyl-2-methylbenzene.TMEDA with

[$RuCl_2(P(OPh_3)_4$] produces not the expected o-xylidene complex but [$RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3$].

Reactions of the lithium salt of 2,3-dimethylnaphthalene with [$RuCl_2P_4$], (P = PPh_2Me or PMe_3), and the lithium salt of 1,2-dimethylnaphthalene with [$RuCl_2P_4$], (P = PPh_2Me or PMe_2Ph) result in complexes analyzing as [$Ru(CH_2C_{10}H_6CH_2)P_3$], complexes which contain a naphthoquinodimethane ligand.

Reaction of the lithium salt of 1,2-dimethylnaphthalene with [$RuCl_2(PMe_3)_4$] gives two products ; the expected naphthoquinodimethane complex and also the complex [$Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4$].

Mechanisms by which these reactions are thought to occur are discussed.

CHAPTER ONE

1.1 Introduction

It is now three decades since the predictions of Longuet - Higgins [1] and the work of Pettit [2] showed that organic molecules of unusually high instability can be stabilized by coordination to a transition metal.

Pettit's work involved the stabilization of cyclobutadiene, (figure 1.1), and indeed cyclobutadiene is by far the most well known example of this class of ligands.

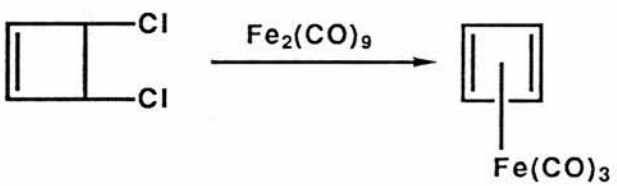


Figure 1.1

By contrast the complex chemistry of the o-xylidene ligand, o-$CH_2C_6H_4CH_2$, which when existing as the neutral o-quinodimethane, is another example of this type of reactive species, has a comparatively short and little - known history. The interest is not only in the complexes themselves, but lies in the potential for releasing the unstable species from the metal, and for this to participate in subsequent reactions, as again shown by Pettit [3] with cyclobutadiene, (figure 1.2).

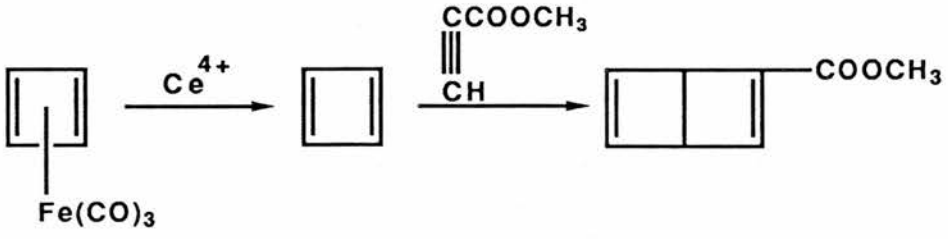
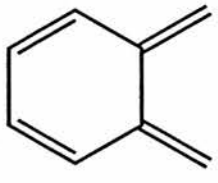


Figure 1.2

This chapter contains a short discussion about o-quinodimethane , describes the methods by which the o-xylidene ligand can bind to transition metals , gives an account of the history of o-xylidene complexes and discusses the analytical methods available for determining the bonding present in any particular complex.

1.2 O-quinodimethane

O-quinodimethane , (**1**) , (figure 1.3) , also called o-xylylene , is a reactive molecule that has been extensively studied both theoretically [4,5] and experimentally [5,6].



(1)

Figure 1.3

Although it is very reactive some direct evidence for its existence has been reported. It has been observed directly by U.V-visible spectroscopy both in solution [7] and in a low temperature matrix [5,8] and by I.R , Raman , fluorescence and fluorescence excitation spectroscopy in a low temperature matrix [8]. The U.V-photoelectron spectrum in the gas phase has also been published [9].

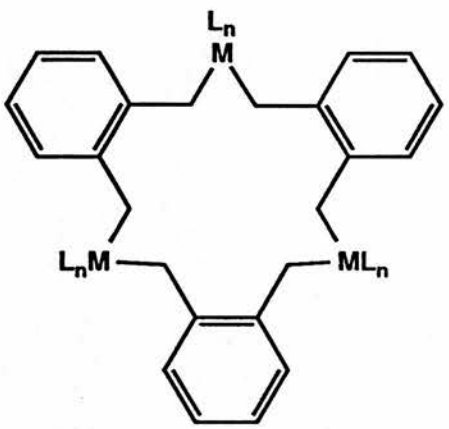
O-quinodimethane as an enophile in the Diels-Alder reaction is very reactive because of the restoration of aromaticity on cycloaddition , and has been utilized for the synthesis of polycyclic ring systems that are otherwise difficult to prepare. The successful applications of the o-quinodimethane intermediate for the syntheses of steroid and alkaloid structures having an aromatic A ring have profoundly aroused the interest of organic chemists [10].

1.3 O-xylidene as a ligand

The umbrella term ' o-xylidene metal complex ' , as coined by Lappert [11] , is used to describe all complexes in which the o-$CH_2C_6H_4CH_2$ ligand is bound to a metal , regardless of the nature of the metal - ligand interaction. The various possible modes are as follows :-

a) bridging as in (2) ,(figure 1.4) , where the ligand donates one

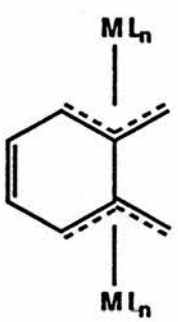
electron to each metal atom.



(2)

Figure 1.4

bridging as in **(3)**, (figure 1.5), where the ligand donates three electrons to each metal atom.

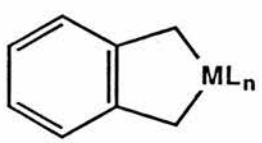


(3)

Figure 1.5

b) chelating , whether in

i) bis (sigma) fashion , (4) , with the ligand donating two electrons to the metal and derived from either the biradical , (5) , or the dianion , (6) , (figure 1.6).



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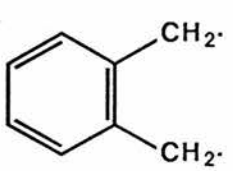

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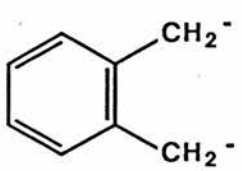
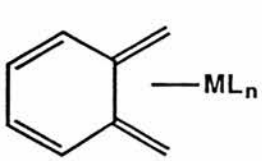


(6)

Figure 1.6

ii) tetrahapto - fashion , (7) , with the ligand donating four electrons to the metal and derived from o-quinodimethane , (8) , (figure 1.7).



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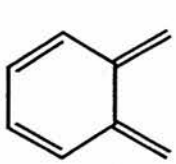


(8)

Figure 1.7

iii) some intermediate state.

The observation of all of these bonding modes in different complexes, and its presence in complexes in which the formal oxidation state of the metal ranges from 0 - VI, testifies to the versatility of o-xylidene as a ligand.

1.4 Metallacyclic sigma-bonding

For a simplified view of the metallacyclic bonding picture we must consider the orbitals of the participating carbon atoms separately, and neglect any geometrical restrictions on the bonding, caused by the requirement of having more than one carbon atom bonding to the metal.

The bonding scheme for an M - CH_2 σ-bond may be accounted for by sharing of the electrons between the transition metal and the carbon atom, (figure 1.8).

Figure (**9**) shows a Molecular Orbital diagram for M - C σ-bond formation between a metal fragment having n ligands L, and an alkyl radical R·, each contributing an electron to form a covalent bond. A metal - alkyl bond of exactly the same nature and energy may be constructed as in figure (**10**), by combination of the L_nM^+ entity with an anionic alkyl group R^-. In this case the

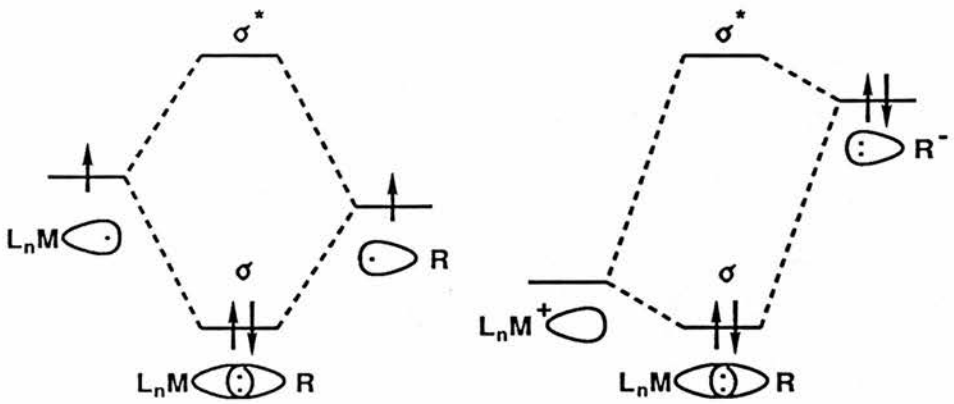


Figure 1.8

carbanionic R group is considered to donate two electrons to the metal. The initial energy of R^- is higher than that of the R· radical in figure (9) and the energy of L_nM^+ is lower than that of L_nM, but the energy of the resultant L_nMR σ and σ^* orbitals should be identical with those in figure (9).

In Valence Bond terms the metal - alkyl σ-bond may be represented by two resonance forms, (figure 1.9).

$$M - R \longleftrightarrow M^+R^-$$

Figure 1.9

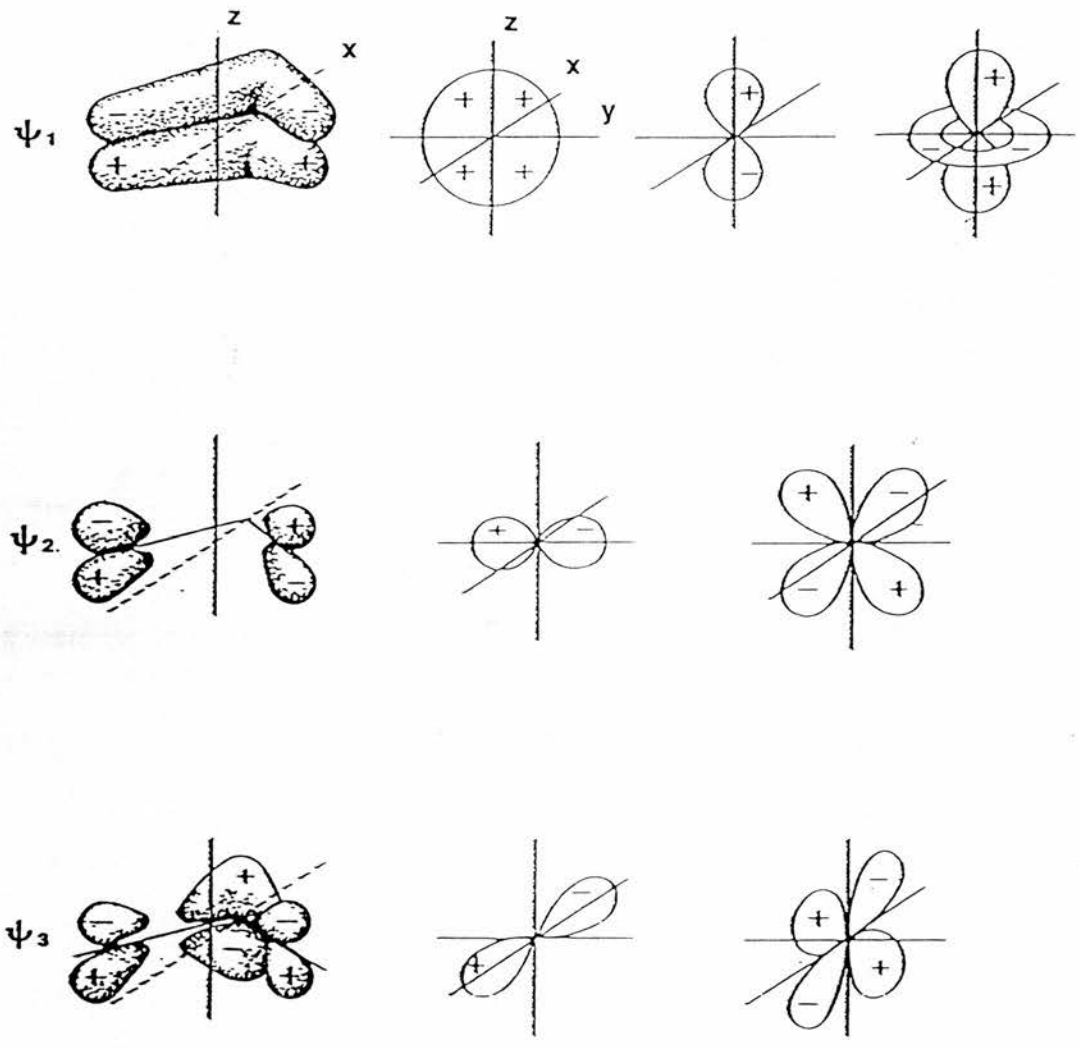
The contribution of each canonical form depends on the nature of the alkyl group as well as that of the metal entity.

1.5 Trihapto-allylic bonding

The three carbons of the π-allyl group form an isosceles triangle and in this configuration the three pπ-orbitals of the allyl group form three molecular orbitals, ψ_1 (bonding), ψ_2 (non-bonding), and ψ_3 (anti-bonding). In the diagram, (figure 1.10), the metal orbitals are shown which can overlap with these ligand group orbitals respectively, below the ψ_1, ψ_2, and ψ_3 orbitals. The ψ_1 orbital overlaps with the metal s, d_{z^2}, p_z orbitals, or hybrid orbitals constructed from them. Similarly the non-bonding orbital, ψ_2, is suitable for overlap with the metal p_y and d_{yz}, or with their hybrid orbitals. The anti-bonding orbital, ψ_3, has the right symmetry to overlap with the p_x and d_{xz} orbitals, or their hybrids to form metal - to - ligand back bonding.

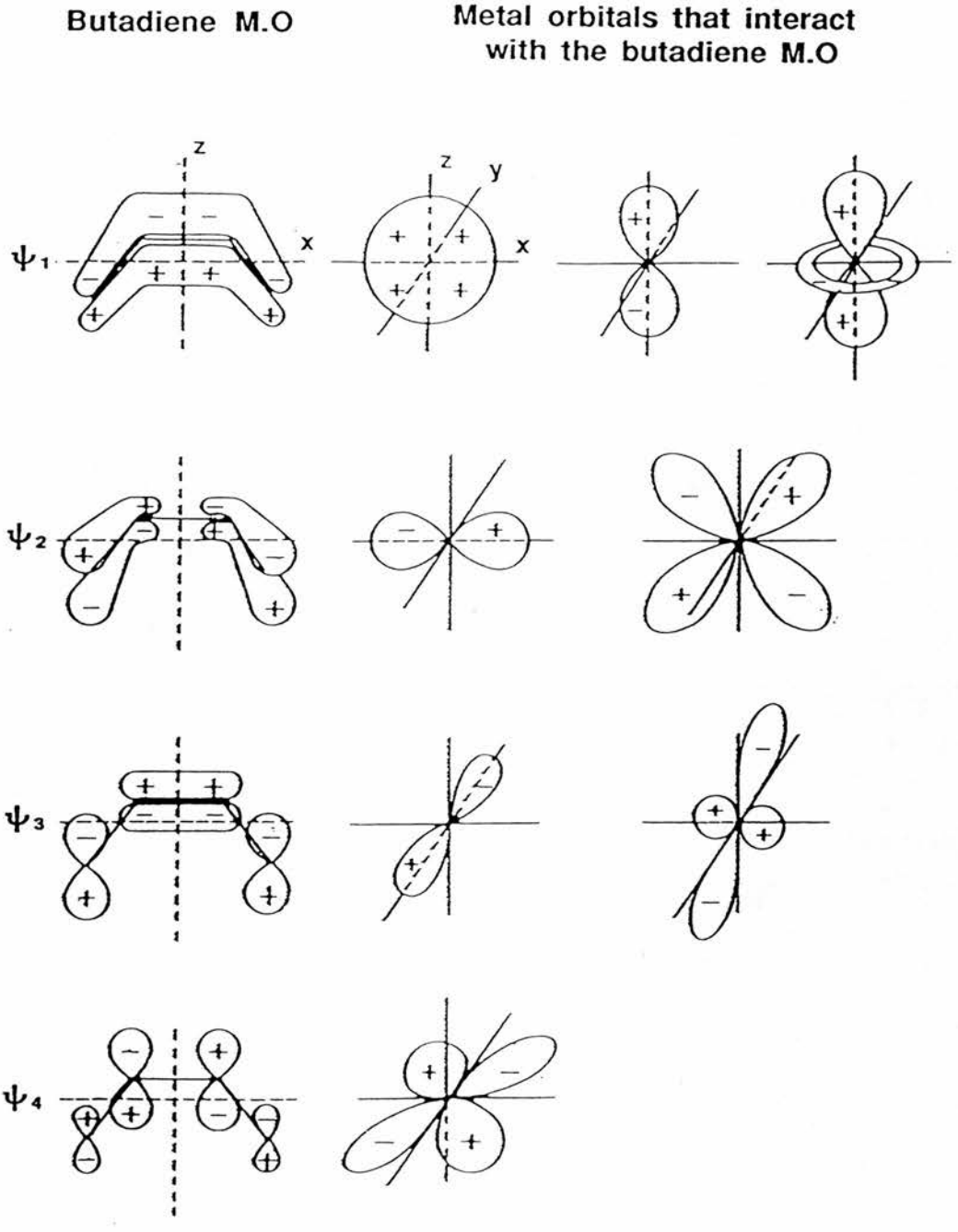
1.6 Tetrahapto-quinodimethane bonding to metals

A description of the bonding of the o-xylidene ligand in an η^4-quinodimethane manner can be simplified by a comparison with the bonding of a metal to butadiene since it is essentially the same fragment involved.



π-Allyl group orbitals ψ_1, ψ_2 and ψ_3, and the corresponding metal orbitals which overlap most effectively with the ligand group orbitals.

Figure 1.10



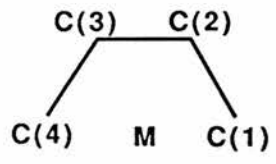
Butadiene molecular orbitals ψ_1 , ψ_2 , ψ_3 and ψ_4 , and the corresponding metal orbitals which overlap most effectively with the ligand orbitals.

Figure 1.11

The butadiene has a cisoid form and the four carbon atoms would be expected to be approximately equidistant from the metal, which lies directly below the plane. The molecular orbitals of the butadiene molecule ψ_1, ψ_2, ψ_3, ψ_4 and their corresponding metal orbitals are shown, (figure 1.11). The ψ_1 and ψ_2 are each occupied by two electrons, whereas ψ_3 and ψ_4 molecular orbitals are unoccupied. It can be seen that the ψ_1 orbital overlaps with the metal s, p_z and d_{z^2} orbitals, or hybrid orbitals constructed from them. Similarly ψ_2 is suitable for overlap with the metal p_x and d_{xz} orbitals. ψ_3 has the right symmetry to overlap with the metal p_y and d_{yz} orbitals, which are available for metal - to - ligand back bonding. The anti-bonding orbital ψ_4 has the correct symmetry to overlap with metal d_{xy} orbital which is also available for metal - to - ligand back bonding.

It is interesting to consider the valence bond description in the light of the previous molecular orbital approach, (figure 1.12).

Representation (**12**) implies that the electrons are localized as in butadiene, with two π - metal-alkene bonds. In molecular orbital terms this is consistent with major bonding to the metal by the ψ_1



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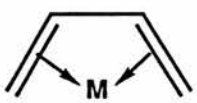

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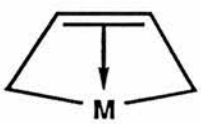


(13)

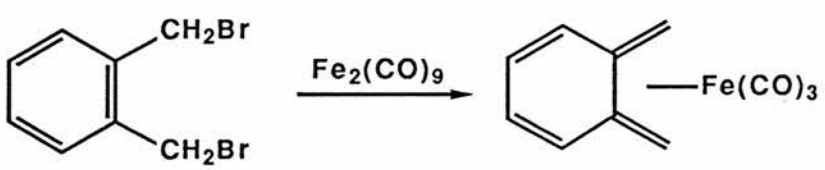
Figure 1.12

and especially the ψ_2 orbitals of butadiene. Representation (**13**) suggests that there is considerable localization of the bonding between the metal and the terminal carbon atoms of the butadiene (σ-character) , and by the metal and the C(2) - C(3) carbons of the diene (π-character). This interaction can be rationalized by the presence of two σ-metal-CH_2 bonds and one π-metal-alkene bond. It has been argued that in molecular orbital terms representation (**13**) reflects an enhanced contribution of the Lumo ψ_3 by back bonding. Thus poor acceptor ligands such as η^5-C_5H_5 groups favour form (**13**) , and good acceptor ligands , such as carbonyl groups favour form (**12**). The situation is much more complex than this but these postulations are borne out in part as we shall see later.

1.7 Complexes of the o-xylidene ligand

The first report of a transition metal complex involving the o-xylidene ligand was by Roth and Meier in 1967 [12].

1,2-bis(bromomethyl)benzene was refluxed with $Fe_2(CO)_9$ in diethyl ether for 3 hours and from the resultant mixture, compound (**14**), (figure 1.13), was obtained in low yield, (5%).



(14)

Figure 1.13

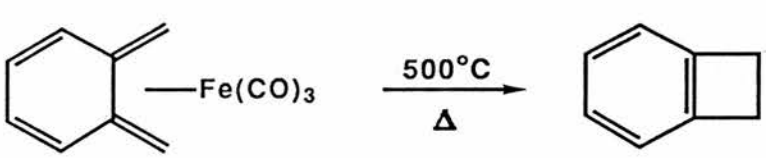
This was identified, firstly by the mass spectrum, which showed peaks at m / e = 244, 216, 188, and 160, corresponding to successive loss of three carbonyl groups, and suggesting then the presence of an $Fe(CO)_3$ group. This left a fragment of m / e = 104, which corresponds exactly to the formula C_8H_8.

The ^1H n.m.r spectrum was unusual in that one of the resonances was at very high field. Since it was thought that the two methylene groups would be equivalent it was realized that the

two doublets observed for these groups (δ 2.20 and δ - 0.05) were resonances of hydrogen atoms on the same carbon atom , and that these hydrogens were inequivalent ($^2J_{HH}$ = 3.2 Hz).

Roth and Meier postulated from this that the $Fe(CO)_3$ was bound in a diene - like fashion , explaining the large chemical shift difference as correlating to the syn (δ 2.20) and anti (δ - 0.05) hydrogens of a diene structure. The complex was compared with that of (butadiene)(tricarbonyl)iron which showed similar resonances (δ 1.68 and δ 0.22 , $^2J_{HH}$ = 2.5 Hz) in the ^1H n.m.r spectrum.

The complex was also shown to have a high thermal stability , a characteristic which is found to be prevalent in many of the compounds containing the o-xylidene ligand. The complex decomposes at 500°C to produce benzocyclobutene (**15**) , (figure 1.14) , a product which would also tend to suggest diene coordination.



(15)

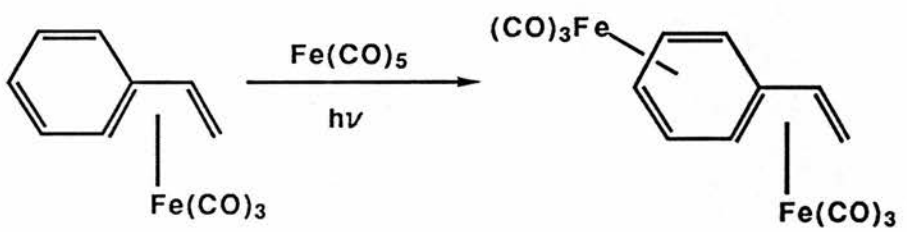
Figure 1.14

Largely , one would suppose , because of the poor yields

obtained , the chemistry of this compound was not really investigated further until 1974.

In 1974 the yield of (**14**) was substantially increased (35%) by reaction of the 1,2-bis(bromomethyl)benzene with $Na_2Fe(CO)_4$ giving the reaction much greater potential [13].

Also in 1974 , Victor and Ben-Shoshan [14] who were involved in the study of the interaction of 4π-electron systems with the $Fe(CO)_3$ fragment , and who had then recently succeeded in taking a tetrahapto-tricarbonyliron complex (**16**) with an 8π-electron conjugated system and adding a further $Fe(CO)_3$ group , (**17**) ,



(16) (17)

Figure 1.15

(figure 1.15) , attempted a similar reaction with the (tetrahapto-o-quinodimethane)tricarbonyliron (**14**) , irradiated in the presence of $Fe(CO)_5$. The reaction was found to give three isomeric $C_8H_8Fe_2(CO)_6$ complexes in comparable yields (figure 1.16).

Formation of (**18**) and (**19**) were described as involving the expected diene type coordination of the residual 4π-electron system while (**20**) involved a redistribution of the π-electron density in the 8π-electron conjugated system.

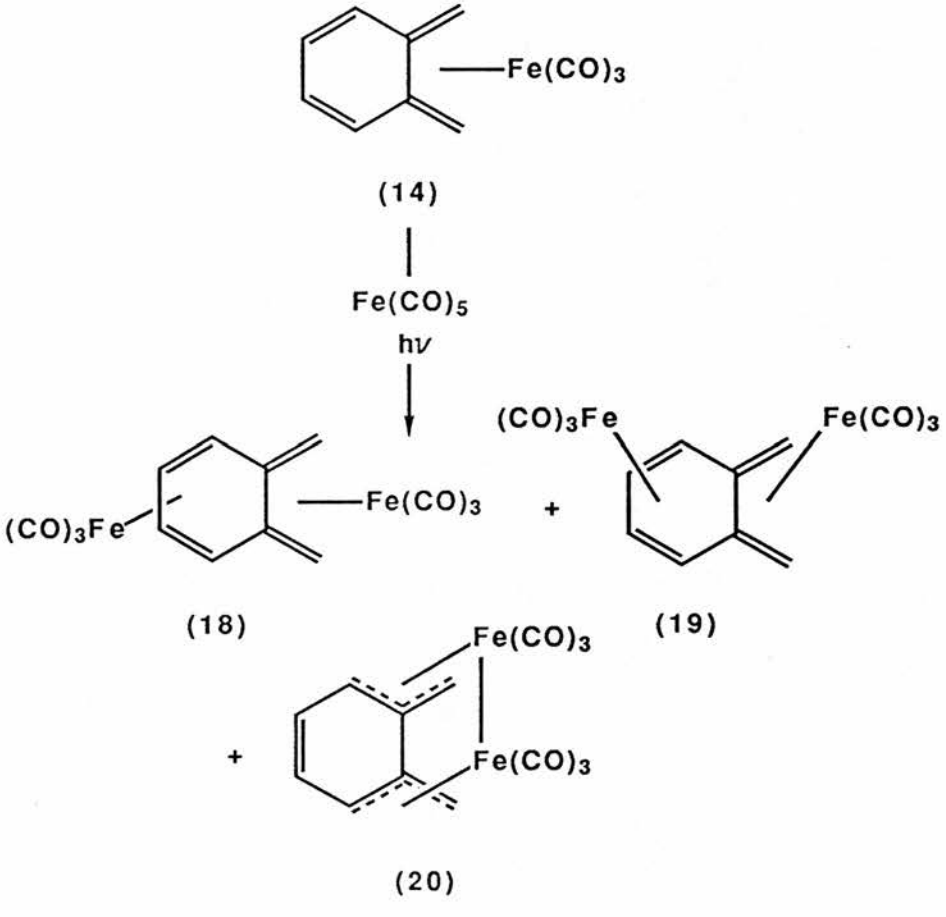


Figure 1.16

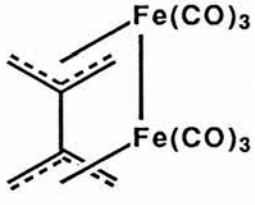
Identification of (**20**) as being bound in a trihapto-fashion was based upon

i) the presence of an uncoordinated double bond in the ligand (ν (C=C) : 1752 cm^{-1}).

ii) the presence of an Fe - Fe bond , as indicated by the mass spectrum (strong peak at m / e 112).

iii) the sp^2 character of the exocyclic carbon bonds as shown by ^{13}C - ^{1}H n.m.r ; J (^{13}C -^{1}H ~ 157 Hz) , which excludes any structure involving C - Fe σ-bonds.

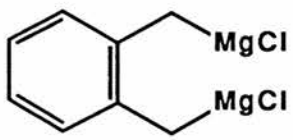
iv) the formation of 1,2-bis(bromomethyl)benzene on bromine degradation , consistent with the formation of 2,3-bis(bromomethyl)-1,4-dibromobutene on similar bromination of (**21**) [15] , (figure 1.17).



(21)

Figure 1.17

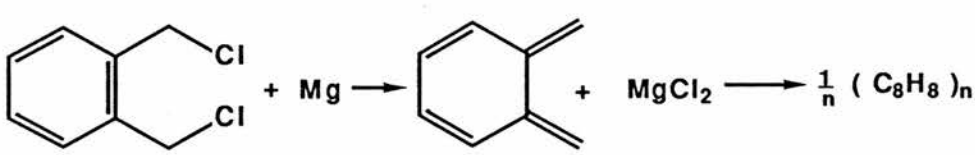
Interest in the o-xylidene ligand was re-awakened in 1980 , partly for the reason that , Lappert and co-workers [16] had by careful optimization of reaction conditions , established a successful high-yield synthesis of the di-Grignard reagent (**22**) , (figure 1.18) , from 1,2-bis(chloromethyl)benzene.



(22)

Figure 1.18

Previous efforts [17] to produce this compound by reaction of the dichloride and magnesium had been relatively unsuccessful with the elimination of $MgCl_2$ and polymerization of the generated o-quinodimethane molecule , (**23**) , (figure 1.19).



(23)

Figure 1.19

It was found that a viable synthesis is critically dependent on a number of constraints.

Firstly it is necessary to use 1,2-bis(chloromethyl)benzene rather than the dibromo compound since the latter results in elimination of $MgBr_2$ no matter the conditions. The use of chlorides rather than bromides is well known , even for simple Grignard reagents , to reduce the extent of the coupling reaction (figure 1.20) [18].

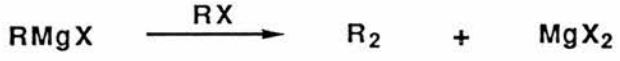
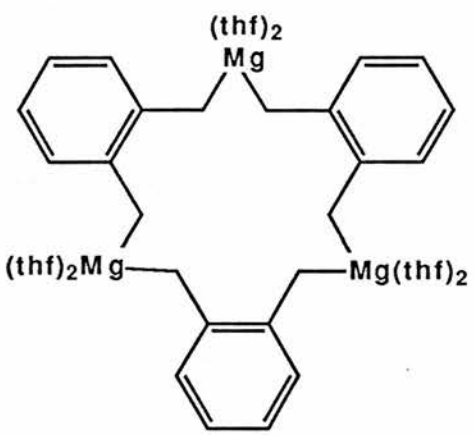


Figure 1.20

Secondly, the use of tetrahydrofuran rather than the more common Grignard solvent, diethyl ether, is essential for high yields. Finally, high dilution is necessary, with the best results obtained when concentrations are about 0.075 mol dm^{-3}. The high dilution simply reduces the probability of a molecular encounter with the 1,2-bis(chloromethyl)organocycle to yield a coupled aromatic product.

Lappert found that cooling of the di-Grignard (**22**) to -40°C produces a colourless, crystalline, extremely air sensitive complex analyzing as [$Mg(CH_2C_6H_4CH_2\text{-}o)(thf)$]. Its infra-red spectrum is indicative of a tetrahydrofuran molecule strongly bound to magnesium; thus the strong ν_{asym} (C - O - C) band of free thf moves from 1069 cm^{-1} to lower wavenumber on coordination [19] (~ 1020 cm^{-1}). The ^1H n.m.r indicates a symmetrically bound o-xylidene, there being a singlet (δ 1.29) corresponding to equivalent methylene groups and equivalent hydrogens within each methylene group, while the aromatic resonances constitute an AA'BB' pattern. The ^1H n.m.r contrasts sharply then with that obtained by Roth and Meier for their

[$Fe(CH_2C_6H_4CH_2\text{-}o)(CO)_3$] compound. The structure for this magnesium compound has not been determined, however, it was soon noticed that solutions of the di-Grignard (**22**) of concentration greater than 0.10 mol dm^{-3} deposited substantial quantities of massive colourless crystals after several days at room temperature. The structural determination established the empirical formula [$Mg(CH_2C_6H_4CH_2\text{-}o)(thf)_2$]. The molecular formula was that of the trimer (**24**), (figure 1.21).



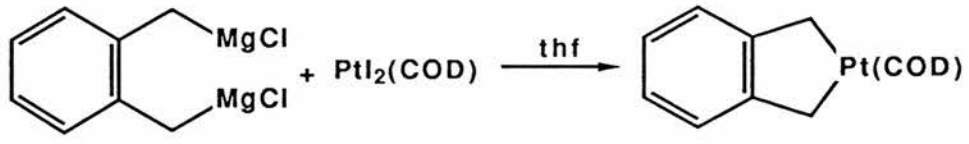
(24)

Figure 1.21

The three magnesium atoms are chemically equivalent as are each of the o-xylidene ligands and the tetrahydrofuran molecules. Each magnesium atom is bridged to the other two magnesium atoms by way of an o-xylidene ligand, so that the system of three

magnesium atoms and three o-xylidene ligand moieties comprises a macrometallacycle.

The utility of the di-Grignard reagent (**22**) as a general organometallic precursor had been realized by many people long before and was now illustrated by the synthesis of [$Pt(CH_2C_6H_4CH_2\text{-}o)(COD)$][16] ,(**25**) ,(COD = cyclo-octa-1,5-diene) , (figure 1.22).



(25)

Figure 1.22

This was prepared by the reaction of the di-Grignard reagent (**22**) and [$PtI_2(COD)$] in tetrahydrofuran. The ^1H n.m.r appeared to be similar to that obtained for the magnesium compounds , there again being a singlet (δ 3.28) corresponding to equivalent methylene groups and equivalent hydrogens within each methylene group , and again contrasting with the Roth and Meier compound (**14**) [12] .

The coupling constant ($^2J(^{195}Pt\text{-}^1H)$ = 92 Hz) for the methylene hydrogens compares favourably to those found in Stone's compounds [20] , [$Pt(CH_2C\{Me\}C\{Me\}CH_2)(COD)$] , (**26**) ,

[$Pt(CH_2C\{Ph\}C\{Ph\}CH_2)(COD)$, **(27)** , and

[$Pt(CH_2C\{=CH_2\}C\{=CH_2\}CH_2)(COD)$] , **(28)** , (figure 1.23) where $^2J(^{195}Pt\text{-}^1H)$ has magnitudes 92 Hz , 86 Hz and 103 Hz respectively.

The ^1H n.m.r of Stone's compounds also showed only a single sharp line with appropriate $^{195}Pt\text{-}^1H$ coupling for the $PtCH_2$

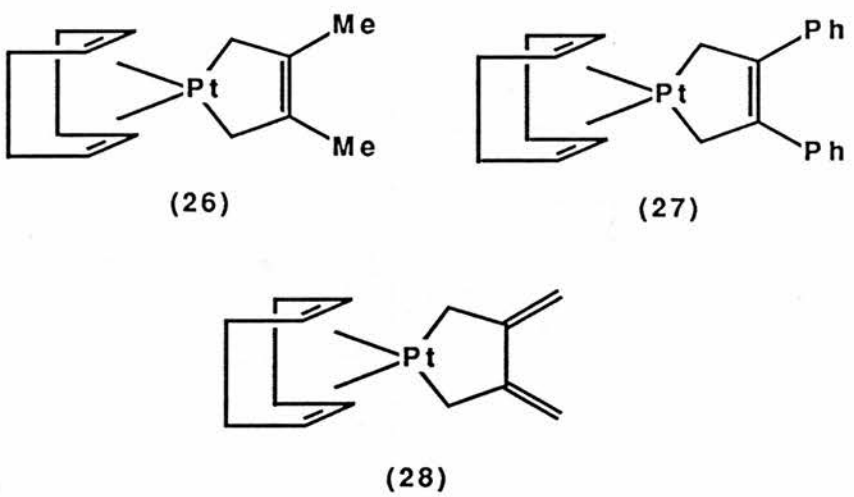


Figure 1.23

hydrogens and interestingly showed no change in the line shape of the signal on cooling to - 90°C. This implied the absence of pseudo-axial and equatorial environments , and hence suggested to Stone the presence of a platinacyclopentene ring with planar geometry. As for the ^1H n.m.r , the $^{195}Pt\text{-}^{13}CH_2$ signal of **(25)** was readily assigned by its intensity and position and again by comparison with Stone's compounds. The coupling constant ($^1J($

^{195}Pt -$^{13}CH_2$) = 795 Hz) , is characteristic of a carbon atom σ-bonded to platinum [21] and is larger than that expected for a platinum atom coupled to olefinic carbons [21]. From these comparisons Lappert concluded that his o-xylidene platinum compound could also be best described as a metallacycle , containing a platinacyclopentene ring. It may be worthwhile at this stage to note that Stone suggested that the formation of (**26**) and (**27**) probably involves the initial formation of a tetrahedral species containing cyclo-octa-1,5-diene and the 1,3-diene as ligands.

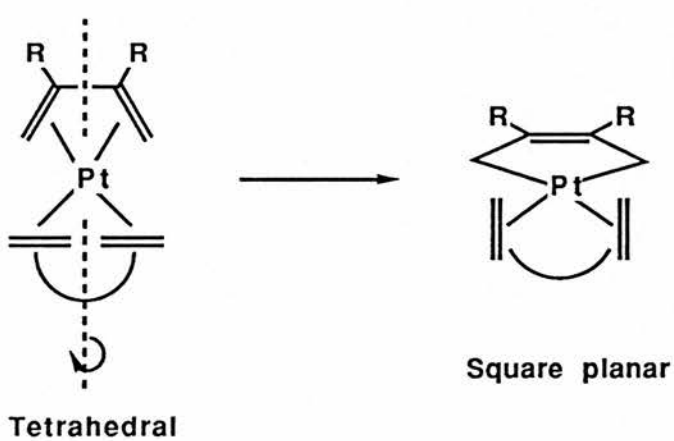


Figure 1.24

Then oxidative transfer of two electrons from platinum to the 1,3-diene with a concomitant twisting process could afford the square-planar platinacyclopentene structure , (figure 1.24).

Lappert next turned his attention to the early transition metals , specifically those of titanium [22,24] , zirconium [22,24] , hafnium [22,24] ,

and niobium [23,24] in oxidation states + 4.

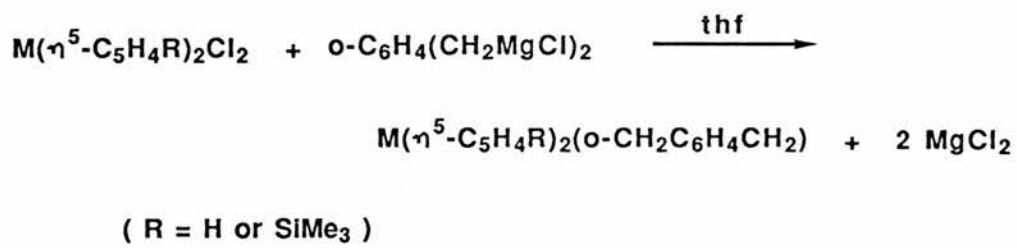
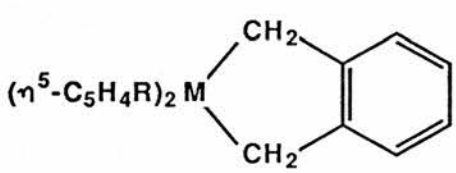


Figure 1.25

He used as his starting materials a tetrahydrofuran solution of the di-Grignard reagent (**22**) and the appropriate metallocene(IV) chloride , (figure 1.25).



(29) ; M = Ti, R = $SiMe_3$
(30) ; M = Zr, R = $SiMe_3$
(31) ; M = Hf, R = $SiMe_3$
(32) ; M = Nb, R = $SiMe_3$
(33) ; M = Ti, R = H
(34) ; M = Zr, R = H
(35) ; M = Hf, R = H

Figure 1.26

Each of the metallocene(IV) chlorides used gave the expected

products , (figure 1.26).

The complexes showed remarkable thermal stability , melting without decomposition at up to 177°C. This contrasts with the behaviour of other d^0 metallacycles. $[Ti(\eta^5\text{-}C_5H_5)_2(CH_2)_4]$ decomposes rapidly even at 0°C [25]. ^1H and ^{13}C n.m.r data was again comparable with that obtained for the platinum complex and the complexes were described as metallacycles. Structural data was said to confirm this finding.

The analogous $[Zr(\eta^5\text{-}C_5H_5)_2(CH_2C\{Me\}C\{Me\}CH_2)]$ as prepared by Erker and co-workers [26] has in fact been postulated as containing η^4-binding. It may be asked why apparently similar compounds have been described as containing different modes of bonding.

Erker noted that the room temperature ^1H n.m.r spectrum of his compound also exhibited equivalency of the methylene groups similar to that observed by Lappert. At low temperature however the hydrogens of the methylene groups were " frozen out " and he saw a pattern similar to that observed by Roth and Meier for their iron xylidene , he thus described his compound as containing η^4-binding , or more specifically σ^2,π-binding.

Erker explains the equivalency of the hydrogens on the methylene groups as being due to rapid migration of the Cp_2Zr unit from one face of the diene ligand to the other via an intermediate metallacyclopentene (figure 1.27).

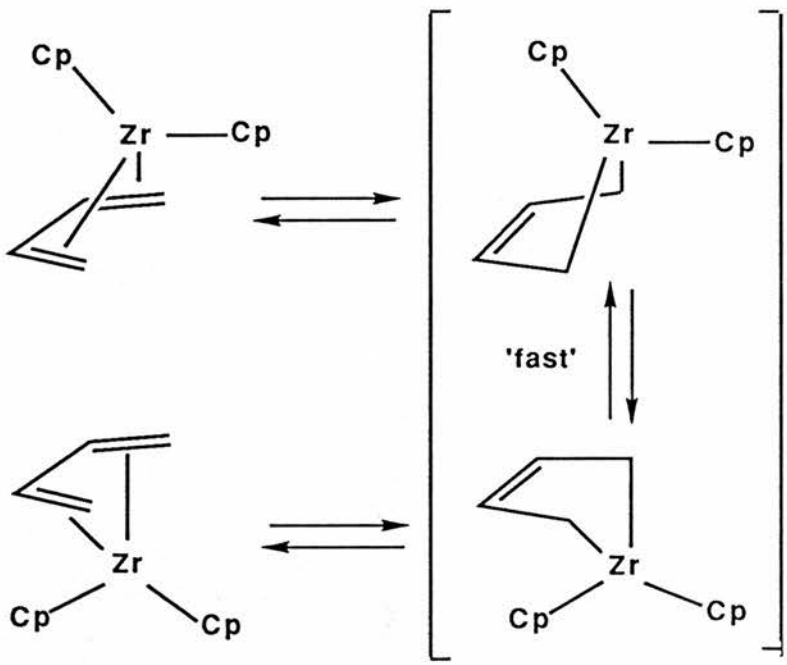


Figure 1.27

Lappert's explanation for the equivalency of the hydrogens of the methylene groups would also seem to explain the resonances seen at low temperature. He states that in the solid state the metallacyclopentene unit is not planar but contains a fold which is probably present in solution , whence magnetic inequivalence of the two cyclopentadienyl ligands is to be expected as well as for the CH_2 hydrogens (pseudo-axial and pseudo-equatorial). However at room temperature such inequivalence in the solution n.m.r spectra of the complexes is not observed because of rapid interconversion of the two environments as shown (figure 1.28).

On closer inspection the two explanations would seem to support

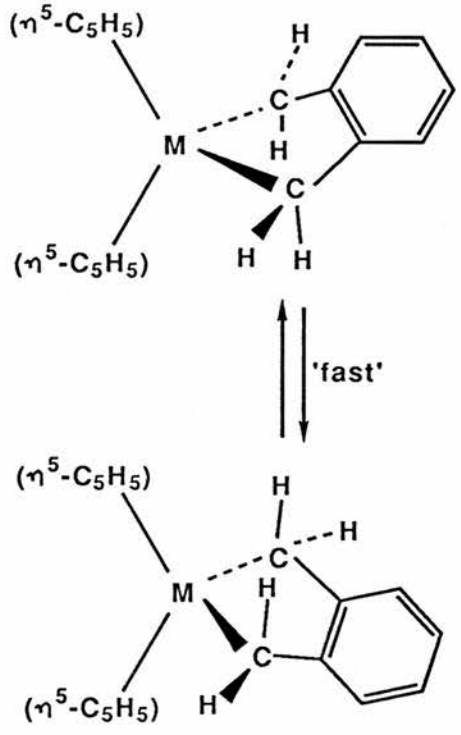


Figure 1.28

one another and to suggest that metallacyclic coordination is just a limiting situation of the σ^2,π-resonance form of η^4-binding.

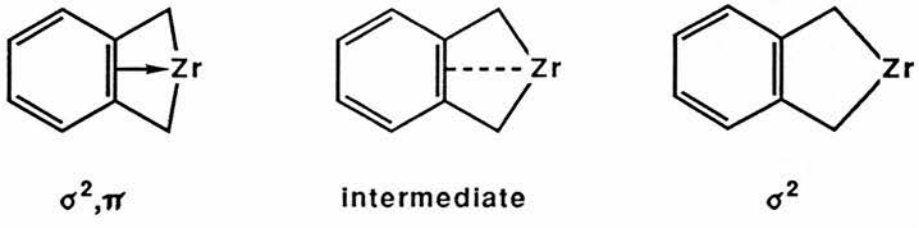
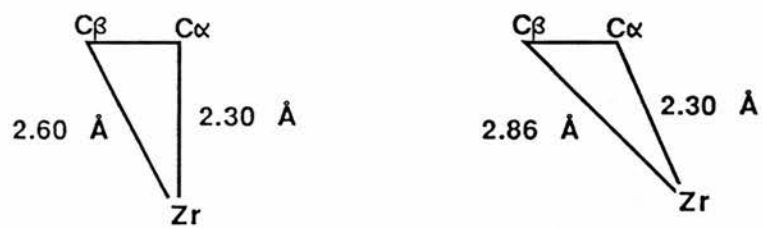


Figure 1.29

This interpretation would seem to be in accord with the

observed bond lengths Zr - Cα and Zr - Cβ of both Erker's and Lappert's compounds and explain how

[$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C_6H_4CH_2\text{-}o)$] , (**34**) can be classed as a metallacycle, while [$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C\{Me\}C\{Me\}CH_2)$] is classed as containing η^4-binding , (figure 1.29). The Zr - Cα bond lengths for both [$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C_6H_4CH_2\text{-}o)$] , (2.30 Å) and [$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C\{Me\}C\{Me\}CH_2)$] , (2.30 Å) are appropriate to a carbon atom σ-bonded to zirconium. The Zr- C σ-bond is best typified by the value of 2.283 Å in [$Zr(\eta^5\text{-}C_5H_5)_2Me_2$] [27].



σ^2,π (36)

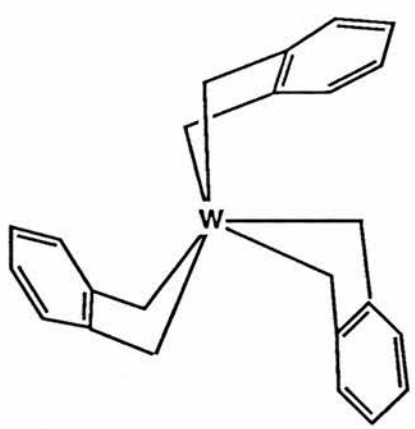
σ^2 (37)

Figure 1.30

The Zr - Cβ distances are much longer. Zr - Cβ for [$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C_6H_4CH_2\text{-}o)$] , (2.86 Å) , may be considered as non-bonding and then we have just the σ^2-metallacyclic situation (**36**) , Zr - Cβ for [$Zr(\eta^5\text{-}C_5H_5)_2(CH_2C\{Me\}C\{Me\}CH_2)$] ,

(2.60 Å) , may be considered as weakly bonding , and characteristic of π-bonding and then we have the σ^2,π-resonance form of η^4-binding , (**37**) , (figure 1.30).

Lappert's next objective was to explore the possibility of stabilizing metal complexes in even higher oxidation states than the +4 already achieved. It was noted that o-$CH_2C_6H_4CH_2$ is sterically rather undemanding when functioning as a chelating ligand with a relatively small ' bite ' angle (CH_2 - M - CH_2) ~ 77°. It had certainly proved possible with the catecholate , o-$OC_6H_4O^{2-}$ ligand , which is isoelectronic with o-$CH_2C_6H_4CH_2$ to arrange three of these around a metal (III) centre as in [$M(OC_6H_4O\text{-}o)_3]^{3-}$, (M = Cr or Fe) [28].

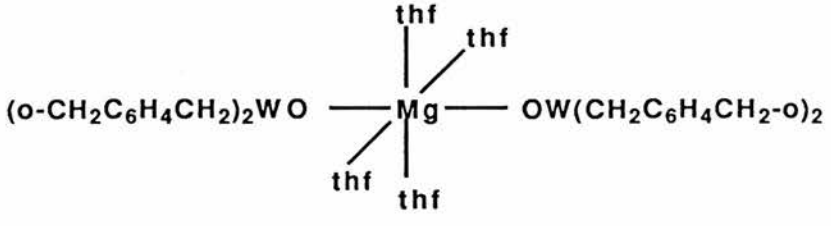


(38)

Figure 1.31

The aim of the work then was to prepare the tris(chelate) metal

complexes of the Group 6 transition metals , particularly the tungsten compound (**38**) , (figure 1.31) , which was expected to be the most readily accessible of this family. The nature of the complex [11,29] derived from the reaction of the di-Grignard reagent (**22**) or [$Mg(CH_2C_6H_4CH_2$-o)(thf)] with [WCl_4O] is critically dependent on the reaction conditions. The optimum yield for isolation of the reduced species [$\{W(CH_2C_6H_4CH_2$-o$)_2O\}_2Mg(thf)_4$] , (**39**) , (figure 1.32) , was achieved by adding 3.3 mol equiv.s of (**22**) to [WCl_4O] in thf at - 78°C.



(**39**)

Figure 1.32

A reaction temperature above 20°C gave mixtures of (**38**) and (**39**). The use of less than 3.3 mol equiv.s resulted in reduced yields of (**39**) from ca. 35% to traces at 3.0 mol equiv.s . Reproducible procedures for the synthesis of the tris(chelate) , (**38**) , typically in 35% yield required use of greater than ca. 3.5 mol equiv.s . There is ambiguity in assigning (**38**) as a metal (VI) since the mode of bonding is again not well defined. In extreme

formulations the complex may be regarded as derived from (**6**) and W(VI) or from (**8**) and W(0). Lappert prefers to regard complex (**38**) as W(VI) because on reduction it gives a tungstate (V) analogue. The considerable thermal stability of (**38**) is demonstrated by its being sublimable at ca. 160°C (10^{-2} Torr). [WMe_6] is thermally unstable and decomposes at - 25°C [30,31]. Assignment of ^1H n.m.r data was aided by comparison with the published data for Roth and Meier's compound. The notable feature is the doublet for the syn hydrogens (δ 2.49) and the doublet for the anti hydrogens at high field (δ - 0.39), the two methylene groups being equivalent. The ^1H n.m.r would tend to suggest some degree of π-interaction. Lappert in fact described the bonding as intermediate between σ-metallacyclic and η^4-quinodimethane.

The compound [$Mo(CH_2CHCHCH_2)_3$] [32] has also been synthesized and has been described as containing η^4-bonding. A comparison of the M - Cα and M - Cβ bond lengths as with the zirconium shows that Mo - Cα and Mo - Cβ bond lengths are equal, (2.29 Å), and hence the molybdenum atom lies directly below, and equidistant from the carbon atoms of the $CH_2CHCHCH_2$ ligand, perfectly positioned for maximum π-interaction. The short -long -short bond alternation of the ligand is the same as that of butadiene itself and the interaction we are seeing is quite clearly η^4- or more specifically π^2-bonding (**40**), (figure 1.33). In the

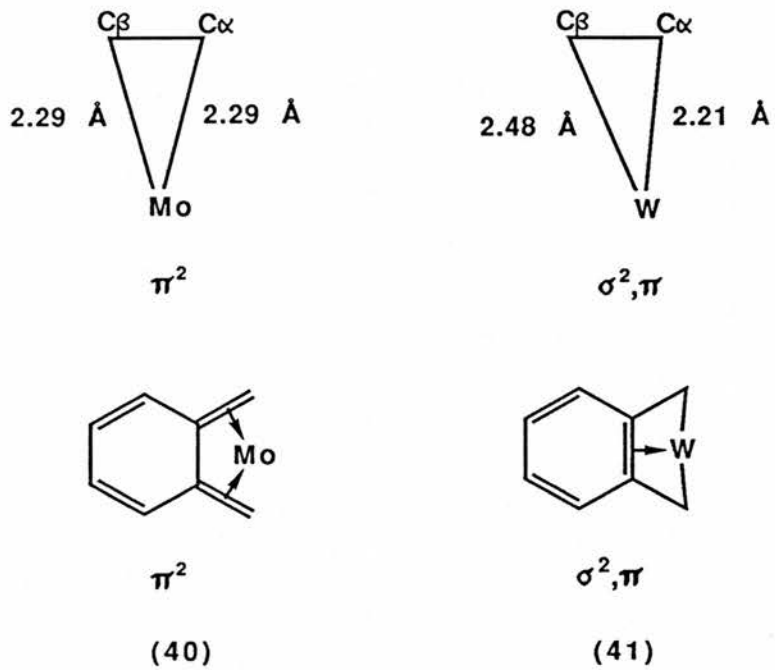


Figure 1.33

tungsten tricycle the W - Cα bond length , (2.21 Å) , is appropriate to a carbon atom σ-bonded to tungsten and the slightly longer W - Cβ , (2.48 Å) suggests a weak π-interaction and thus we have the familiar σ^2,π-interaction (**41**).

We have now summarized the bulk of the quite considerable amount of work carried out by Lappert on the use of of the di-Grignard reagent (**22**) in the synthesis of o-xylidene complexes.

Cole-Hamilton's early research on o-xylidene complexes was carried out about the same time as Lappert's. Whilst many of the objectives were the same , the chemistry involved a different

approach.

A few systems have been reported in which activation of saturated hydrocarbons by soluble transition metal complexes occur , but often the reactions are inefficient. On the other hand very many reactions where oxidative addition of C - H bonds of coordinated phosphines , amines etc. occurs , have been observed. These are called cyclometallation reactions. As a bridge between cyclometallation and direct activation of hydrocarbons Cole-Hamilton was interested in the possibility of forming metallacycles from metal alkyl complexes. Now usually , alkyls decompose by β-elimination [33] although reductive elimination can occur [33]. Other decomposition modes that have been observed are α-hydrogen abstraction [34] to give an alkane and a carbene or γ-hydrogen [35,36] abstraction to give a metallacyclobutane and an alkane. It occurred to Cole-Hamilton however that since 5-membered rings have the least ring strain , δ-hydrogen abstraction might be feasible. It was decided therefore to investigate the o-methylbenzyl ligand [37].

Reaction of [o-$CH_3C_6H_4CH_2MgBr$] , (**42**) , with [$PtCl_2(COD)$] and PEt_3 afforded white crystals of [cis-$Pt(PEt_3)_2(CH_2C_6H_4CH_3)_2$] , (**43**). When this complex was refluxed in xylene for several hours a new compound [$Pt(CH_2C_6H_4CH_2$-o$)(PEt_3)_2$] , (**44**) , (figures 1.34 and 1.35) , was isolated as white crystals. In the ^1H n.m.r spectrum , apart from multiplets arising from coordinated triethylphosphine

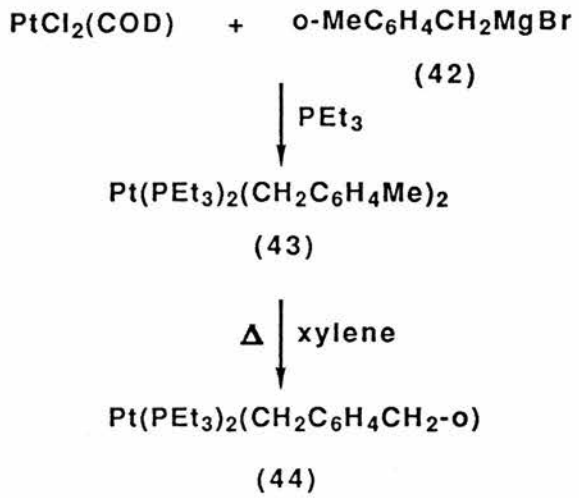
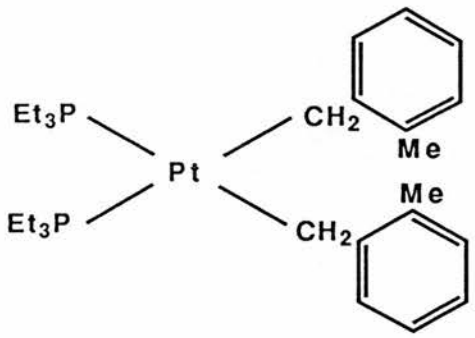


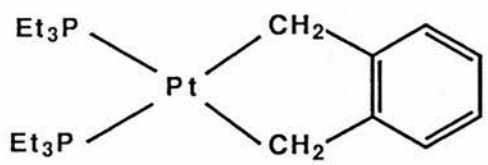
Figure 1.34

the only high - field resonance is an apparent quartet (δ 3.55) flanked by satellites.

All the n.m.r evidence would tend to suggest a metallacyclic structure similar to that of Lappert's platinum compound. The coupling constant ($^{2}J(^{195}Pt\text{-}^{1}H)$ = 66 Hz) is typical of of values found for cis-dialkylbisphosphine complexes of platinum [38], $[Me_2Pt(PPh_2Me)_2]$ [39], (68 Hz), $[(Me_3SiCH_2)_2Pt(PMe_3)_2]$, (73 Hz) [40]. Correlation between $^{1}J(^{195}Pt\text{-}^{13}C)$ values of different platinum complexes is not precise but the value found for **(44)**, (620 Hz), compares much more favourably with the values found for $[(Me_3SiCH_2)_2Pt(PMe_3)_2]$, (528 Hz) [40] and $[Me_2Pt(PMe_2Ph)_2]$, (594 Hz) [41], in which the platinum is bound in a σ-manner to the carbons, than with the value for the complex $[(C_2H_4)Pt(PPh_3)_2]$,



(43)



(44)

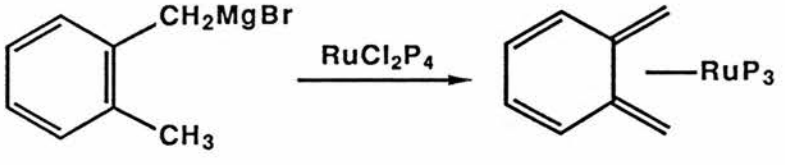
Figure 1.35

(194 Hz) [42] which is bound through the π-bonds of the ethene group. Lastly the phosphorus - carbon coupling $^{2}J(^{31}P\text{-}^{13}C)$ interpreted as ($^{2}J(^{31}P\text{-}^{13}C_{trans}) = 92.4$ Hz and $^{2}J(^{31}P\text{-}^{13}C_{cis}) = 9.0$ Hz) is also consistent with values found for cis-dialkylbis phosphine complexes of platinum, $[(Me_3SiCH_2)_2Pt(PMe_3)_2]$ [40], ($^{2}J(^{31}P\text{-}^{13}C_{trans}) = 94.1$ Hz and $^{2}J(^{31}P\text{-}^{13}C_{cis}) = 7.7$ Hz), $[(CH_3C_6H_4CH_2)_2Pt(PEt_3)_2]$ [37], ($^{2}J(^{31}P\text{-}^{13}C_{trans}) = 94$ Hz and

$^2J(^{31}P\text{-}^{13}C_{cis}) = 9\,Hz$).

For γ-hydrogen abstraction there is a marked difference between platinum and ruthenium , the former [35] does not react below ~ 160°C whereas for ruthenium [36] reaction occurs below room temperature. Since the synthesis of the platinum metallacycle required refluxing xylene it was thought that the use of ruthenium might ease the requirements of the reaction.

Reactions of [$RuCl_2P_4$] , (P = PMe_2Ph or PPh_2Me) , with [o-$CH_3C_6H_4CH_2MgBr$] gave compounds analyzing as [$Ru(CH_2C_6H_4CH_2\text{-}o)P_3$] [43] , (**45**) , (figure 1.36) , even at 0°C. However the ^1H n.m.r showed the familiar ' frozen ' pattern of the syn and anti hydrogens consistent with η^4-binding and not metallacyclic coordination.



(45)

(P = PMe_2Ph or PPh_2Me)

Figure 1.36

Structural analysis confirms the η^4-binding as being intermediate between the resonance forms σ^2,π- and π^2- .The result is not that

surprising when one reflects that all the complexes of the Group 8 metals , Fe , Ru , and Os containing either the $CH_2CHCHCH_2$ ligand or the o-xylidene ligand , show η^4-binding , and this perhaps demonstrates the inability of Fe , Ru and Os to participate in metal - ligand back - bonding in these instances. Further details of this ruthenium work are discussed in chapters two and three.

Stimulated interest in the o-xylidene ligand resulted in a number of publications in 1981 - 1982.

It was Bergman's idea to synthesize a dimetallacycle [44] , that is a metallacycle containing two metals , so that comparisons with the more numerous mononuclear metallacycles could be made. For this end he chose to prepare , after careful consideration , a complex which would include the o-xylidene ligand.
The metallacycle synthesis used , was based on that previously employed to prepare a variety of bis(μ-carbonyl)bis(η^5-cyclopentadienyl)dicobalt metallacycles [45]. Thus addition of tetrahydrofuran to a 1.5 : 1 mixture of solid 1,2-bis(bromomethyl)benzene and the dinuclear radical anion , (**46**) , gave the neutral compound [$((\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO))_2$] and (**47**) , (figure 1.37). Support for the structure shown for (**47**) was obtained by comparison of I.R and n.m.r spectral data to that obtained for other known dialkyl dicobalt compounds.Thus the I.R

band at 1811 cm^{-1}, singlets in the ^1H n.m.r due to the methylene,

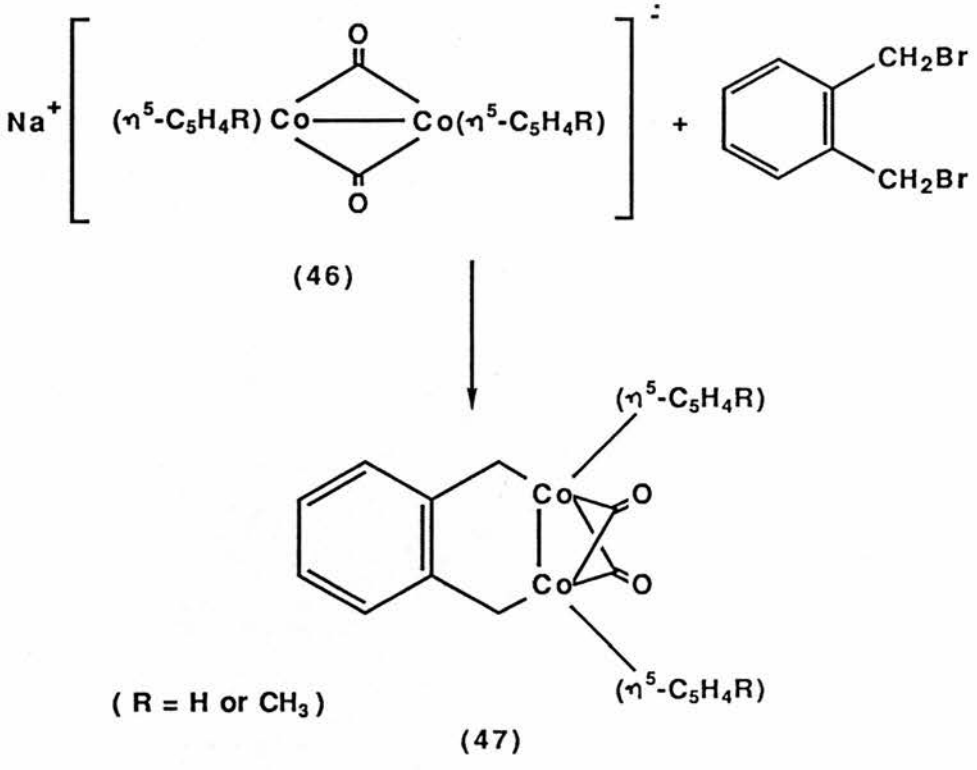
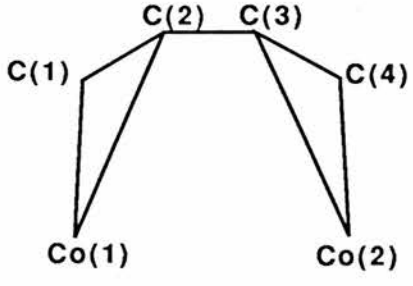


Figure 1.37

(δ 1.57), and cyclopentadienyl hydrogens, and the aromatic resonances that are typical of o-dialkylbenzenes, all pointed toward a symmetrical dimetallacycle containing bridging carbonyl ligands. Closer examination of the ^1H n.m.r showed that on cooling, broadening of the methylene resonance was followed by its virtual disappearance between - 30°C and - 50°C and the appearance of the now familiar doublets, (δ 2.71 , δ 0.22), at - 80°C. Bergman

suggested a ring flipping mechanism consistent with that which we have previously described , (figure 1.28) . He was concerned whether in fact his compound would be more accurately be described as a π-complex than as a metallacycle. He suggested that the formulation would require on the basis of the effective atomic number rule that there be no cobalt - cobalt bond. Structural analysis on the analogous compound $[(\eta^5\text{-}C_5H_4CH_3)_2(CH_2C_6H_4CH_2)(\mu\text{-}CO)_2Co_2]$ showed that there is a Co - Co bond. In addition the Co(1) - C(2) and Co(2) - C(3) distances average 2.98 Å and are clearly non-bonding ,(the bonding Co(1) - C(1) and Co(2) - C(4) distances are both 2.08 Å) , (**48**) , (figure 1.38). The bonding is therefore best described as metallacyclic.



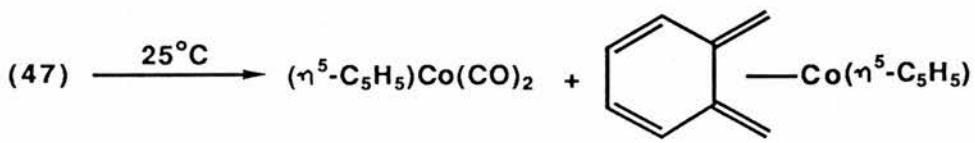
Co(1) - C(1)	2.08 Å
Co(1) - C(2)	2.98 Å
Co(2) - C(3)	2.98 Å
Co(2) - C(4)	2.08 Å

(48)

Figure 1.38

Having established the structure of (**47**) Bergman showed that solutions of (**47**) that were allowed to stand at room temperature slowly changed colour from dark green to red. Repetition of this

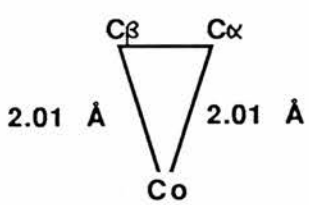
decomposition on a preparative scale resulted in isolation of a compound analyzing as [$Co(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)$] , (**49**) , (figure 1.39).



(49)

Figure 1.39

Just as application of the effective atomic number rule predicted that (**47**) was a σ-complex , it was expected that , (**49**) , would be a π-complex.



(50)

Figure 1.40

The ^1H n.m.r showed the two doublets , (δ 2.65 , δ - 0.54) , due to the ' frozen ' methylene hydrogens. Structural analysis also confirms the π-bonding formulation ,with all four Co - C(xylidene)

distances essentially equal , (2.01 Å) , (**50**) , (figure 1.40). In an attempt to prepare a dinuclear π-complex of o-xylidene , Bergman briefly examined the photochemistry of (**47**) , since the loss of one carbonyl would in principle give the desired compound. His work on this was , unfortunately not very successful. Vollhardt [46] has since shown that irradiation of [$Co(CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)$] , (**51**) , which is analogous in all respects to Bergman's mononuclear o-xylidene complex , produces , in the presence of

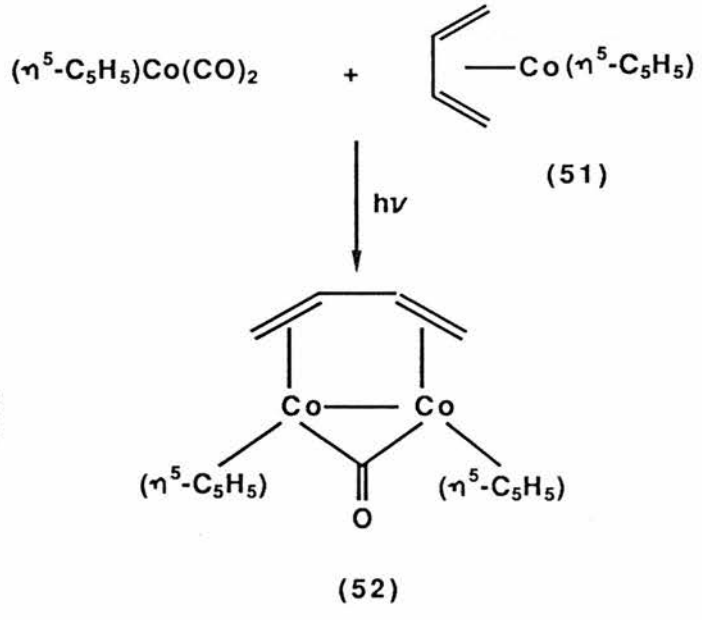
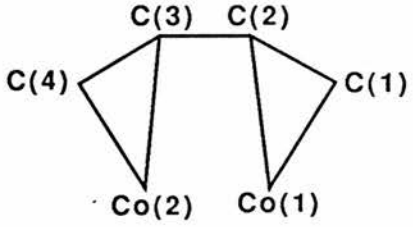


Figure 1.41

[$(\eta^5\text{-}C_5H_5)Co(CO)_2$] , a dinuclear complex

[$(CH_2CHCHCH_2)(CO)(\eta^5\text{-}C_5H_5)_2Co_2$] , (**52**) , (figure 1.41) , which

by spectroscopic and structural analysis can be described as a π-complex. Thus the I.R spectrum exhibits the anticipated bridging carbonyl stretching absorption at 1782 cm^{-1}. In the ^1H n.m.r the methylene hydrogens appear as signals centred at δ 1.94 and δ -0.78.



(53)

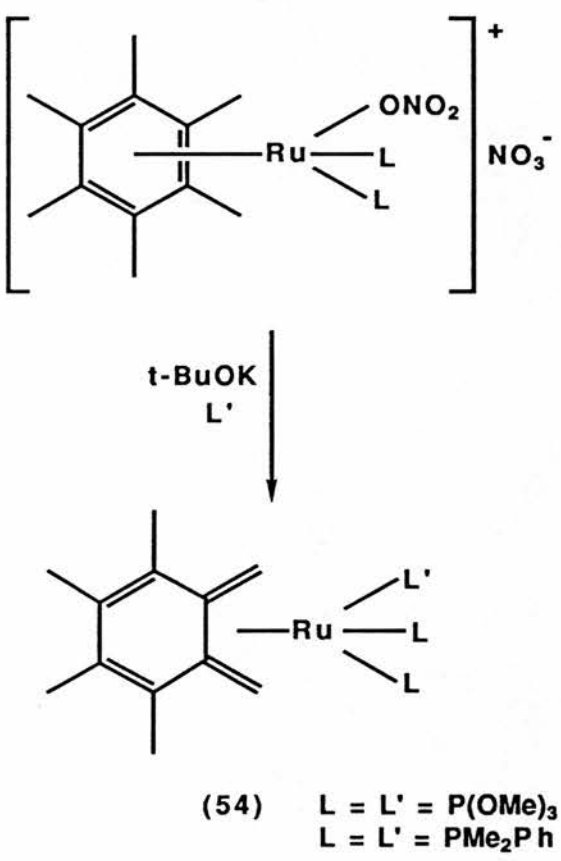
Co(1) - C(1)	2.02 Å
Co(1) - C(2)	2.04 Å
Co(2) - C(3)	2.04 Å
Co(2) - C(4)	2.02 Å

Figure 1.42

The X-ray structure shows bond alternation in the $CH_2CHCHCH_2$ ligand, (short - long - short) , similar to that in butadiene and Co - C($CH_2CHCHCH_2$) distances approximately equal, (Co(1) - C(1) and Co(2)-C(4) 2.02 Å , Co(1) - C(2) and Co(2) - C(3) 2.04 Å) , **(53)** , (figure 1.42). Vollhardt's work would seem to indicate a dinuclear π-xylidene as being intermediate in the conversion of the dimetallacycle to a mononuclear π-xylidene and shows that metallacyclic coordination can be converted to η^4-binding with relatively slight structural changes, a fact which we have also suggested previously.

The next reports of interest were two publications which contained further work on ruthenium o-xylidenes. The work is particularly interesting since both papers cite similar synthetic methods but produce quite startlingly different products.

Bennett [47,48] carried out a double - deprotonation of a

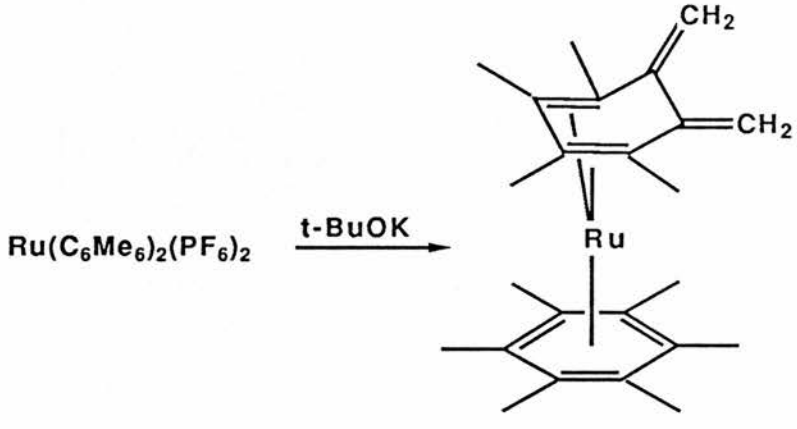


(54) L = L' = $P(OMe)_3$
L = L' = PMe_2Ph

Figure 1.43

η^6-hexamethylbenzeneruthenium(II) complex in the presence of phosphite or phosphine and produced o-xylidene complexes , (**54**) , (figure 1.43) , which he compared with Cole-Hamilton's ruthenium compounds , having comparable spectral data. Mono - protonation of the complexes produced η^3-allylic complexes which compared to the generation of η^3-allyliron(II) complexes by protonation of $FeL_3(\eta^4$-diene) compounds and so also supported the formulation of the complexes as containing η^4-bonding.

Gladfelter [49] reported a similar double - deprotonation of a η^6-hexamethylbenzeneruthenium(II). The ruthenium o-xylidene



(55)

Figure 1.44

produced , (**55**) , (figure 1.44) , in contrast to all previously

identified η^4-quinodimethanes, which are seen to preferentially bind to the exocyclic double bonds, binds to the endocyclic double bonds of the quinodimethane ligand, confirmation of which is given by the structural analysis. It is interesting to note that this is also the first example in which we see significant distortion of the o-xylidene ring with consequent loss of aromatic character and planarity. In the ^1H n.m.r spectrum the methylene hydrogens appear as doublets at δ 5.04 and δ 4.46 which is very close to the normal region for vinyl hydrogens, and quite different from the positions of the corresponding resonances, seen in all the known o-xylidene π-complexes, which appear near Me_4Si.

As seems inevitable in transition metal chemistry, success in producing complexes of a particular metal leads to similar investigations into metals of the same group. This has been the case with ruthenium o-xylidenes. Dixneuf [50,51] has produced a number of iron o-xylidenes (**56**), (figure 1.45), using similar preparative methods to those described by Lappert and Cole-Hamilton. No structural analysis has been possible but the similarities between the spectral properties of these compounds and Cole-Hamilton's establishes without doubt the η^4-nature of the o-xylidene ligand in the compounds. Dixneuf delves much further into the chemistry of the complexes but as we are concerned more with the synthetic and structural analyses of the compounds this will be

omitted.

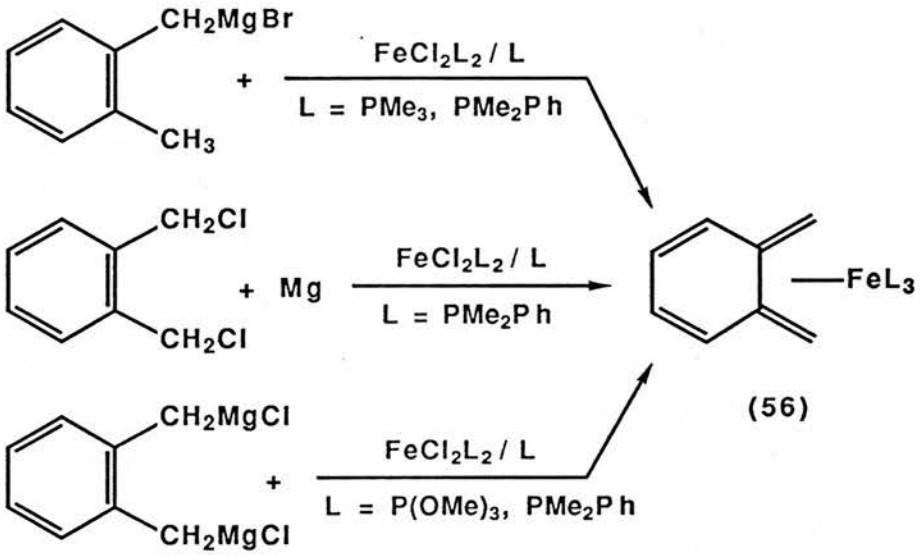


Figure 1.45

Wilkinson [52] has also experimented with synthesizing iron o-xylidenes. In 1985 his work on bis(dimethylphosphino)methane, (dmpm), complexes of iron and ruthenium led him to react the di-Grignard compound (22) with iron(II) acetate in the presence of dmpm , giving a compound analyzing as [$Fe(CH_2C_6H_4CH_2)(dmpm)_2$] , (figure 1.46).

The ^1H n.m.r shows a broad singlet at δ 2.31 and a broad doublet at δ -1.60 for the methylene hydrogens of the o-xylidene moiety. The ^{31}P -{^1H} spectrum shows a broad singlet, a doublet and a broad singlet (relative intensities 1 : 2 : 1) at δ 41.9, δ

-11.5 and δ - 60.5 respectively , indicating the presence of both uni- and bidentate dmpm. The ^1H n.m.r is consistent with a

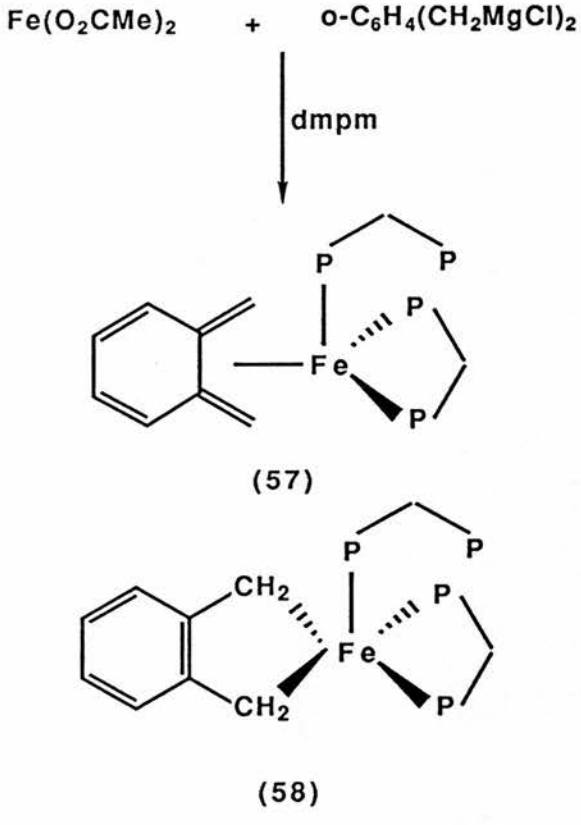


Figure 1.46

π-bonded o-xylidene group. Further the presence of a unidentate dmpm with an uncoordinated phosphorus atom is in accord with an $18e^-$ species , (**57**) , rather than a $16e^-$ species , (**58**).

Wilkinson [53] has also reported preparing an o-xylidene complex [$Fe(CH_2C_6H_4CH_2)(dmpe)_2$] which is claimed to be σ-bonded and

therefore suggests that both the dmpe ligands are bidentate. The ^1H n.m.r shows resonances for the methylene hydrogens at δ 1.91 and δ 1.66 however no further information is available.

The latest report on o-xylidene complexes is by Royo[54] whose group have been involved with the preparation of (η^5-pentamethylcyclopentadienyl)titanium trialkyls and their derivatives.

In this report Royo has reacted [(η^5-C_5Me_5)$TiCl_3$] with [(o-$CH_2C_6H_4CH_2$)$Mg(thf)_2$] in an attempt to prepare [(η^5-C_5Me_5)TiCl(o-$CH_2C_6H_4CH_2$)]. Unexpectedly , the product is found to be solvent dependent. Reaction in toluene does indeed give [(η^5-C_5Me_5)TiCl(o-$CH_2C_6H_4CH_2$)] ,(**59**) ,(figure 1.47) the expected

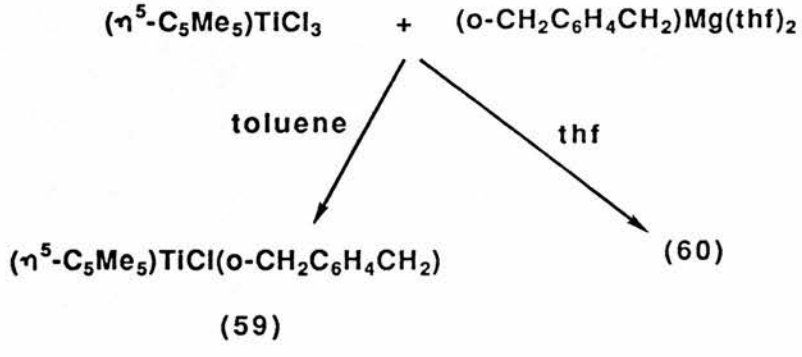


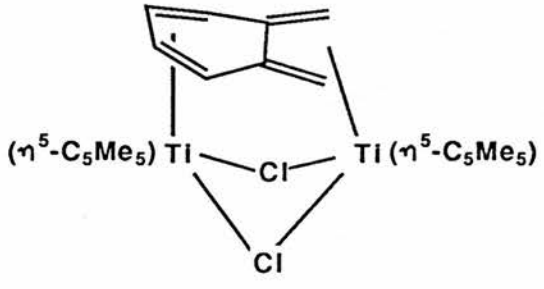
Figure 1.47

product according to Royo's previous results on the facile alkylation of [(η^5-C_5Me_5)$TiCl_3$] with magnesium or lithium

alkyls. The spectroscopic features of (**59**) especially those associated with the methylene unit of the o-xylidene ligand are characteristic of an alkyl derivative.

The ^{1}H n.m.r spectrum shows two doublets centred at δ 1.30 and δ 2.63 with a $^{2}J_{HH}$ coupling constant of 10.5 Hz, the same value as found in [$(\eta^5\text{-}C_5H_5)TiCl(CH_2Ph)_2$], and hence σ-coordination is suggested. The $^{1}J(^{13}C\text{-}^{1}H)$ coupling constant is however somewhat high, (144 Hz).

When the same reaction is carried out in tetrahydrofuran, dark green crystals of (**60**) having the stoichiometry [$((\eta^5\text{-}C_5Me_5)Ti)_2(o\text{-}CH_2C_6H_4CH_2)Cl_2$] can be isolated.The ^{1}H n.m.r



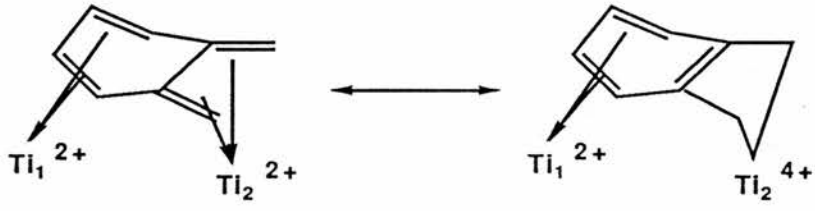
(60)

Figure 1.48

spectrum has resonances at δ 1.19 and δ 0.55 ascribable to the methylene hydrogens and two multiplets centred at δ 3.16 and δ 3.52 which must originate from the endocyclic hydrogens of the

o-xylidene moiety even though they resonate at an unusually high field. An X-ray study reveals that the o-xylidene group is acting as a bridge between the two Ti atoms.

There is considerable distortion of the o-xylidene ring with subsequent loss of aromatic character and planarity , a situation seen earlier with Gladfelter's ruthenium complex which is also bound to the endocyclic double bonds as seen here , (**60**) , (figure 1.48). The Ti(1) atom is equidistant from the C(5) , C(6) , C(7) and C(8) atoms of the endocyclic diene system and we are clearly seeing



(61) (62)

Figure 1.49

η^4-bonding. As to the question of the interaction between Ti(2) and the C(1) , C(2) , C(3) , C(4) system. The Ti(2) - C(1) and Ti(2) - C(4) distances (2.26 Å and 2.24 Å) are somewhat longer than those in [$(\eta^5\text{-}C_5H_5)Ti(CH_2Ph)_3$] , (2.14 A), and very close to those found in [$(\eta^5\text{-}C_5H_5)_2Ti(o\text{-}CH_2C_6H_4CH_2)$] , (**33**) , in which predominantly σ-bonds were proposed. The distances Ti(2) - C(2) and Ti(2) - C(3) (2.53 Å and 2.49 Å) are significantly longer. Royo has suggested

that this suggests a resonance hybrid between the two forms (**61**) and (**62**) , (figure 1.49). The fold angle (a description of the fold angle will be given later) of 80° has been described by Royo as supporting the σ-character of the C(1) - Ti(2) and C(4) - Ti(2) bonds , and his proposed resonance picture. Although perhaps a question of semantics , spectroscopic and structural data is clearly suggesting a σ^2,π-interaction. It may be argued , therefore , that what we are seeing is simply the σ^2,π-form of η^4-bonding as demonstrated many times throughout this chapter.

1.8 Fold Angle

Whilst a comparison of the bond lengths M - Cα and M - Cβ can

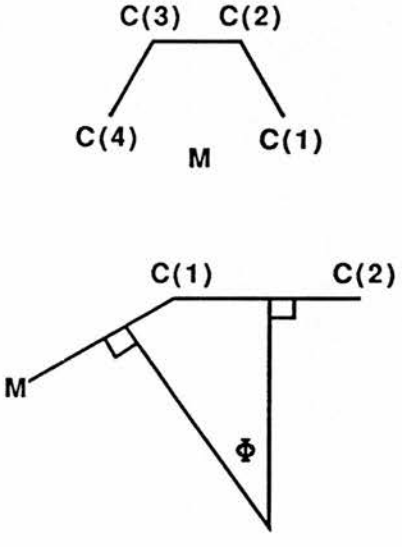
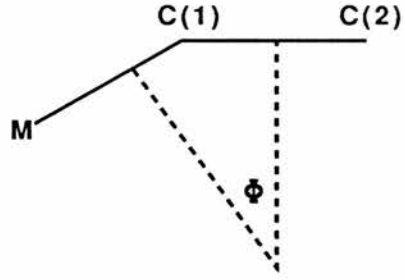


Figure 1.50

be , and has been , used to determine the exact nature of the bonding present in an o-xylidene or $CH_2CHCHCH_2$ complex , a parameter termed the ' fold angle Φ ' is also a useful guide , serving much the same purpose , and taking into account much the same factors. Its advantage lies in its simplicity , consisting of a single value which can immediately be related to the type of bonding present.

The fold angle is defined as being the angle made by the normal to the plane of MC(1)C(4) and the normal to the plane of the four carbon atoms C(1) , C(2) , C(3) , and C(4) , (figure 1.50).

Comparing metallacyclic coordination to the analogous cyclopentene ($\Phi \sim 0^o$) then we should only see a relatively small



Metallacyclic - coordination

Figure 1.51

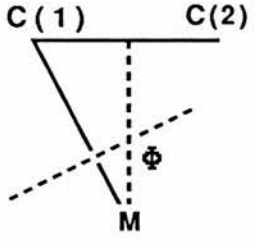
fold angle. We would only expect folding as a consequence of the geometrical requirements of incorporating a large metal atom in a five-membered ring , (figure 1.51).

Compound	Fold Angle (Φ)	Bonding
[$Nb(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_4SiMe_3)_2$]	40°	σ^2
[$Ti(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)_2$]	44°	σ^2
[$Hf(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)_2$]	49°	σ^2
[$Zr(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)_2$]	53°	σ^2
[$Co_2(CH_2C_6H_4CH_2)(CO)_2(C_5H_4CH_3)_2$]	58°	σ^2
[$Zr(CH_2CHCHCH_2)(\eta^5\text{-}C_5H_5)_2$]	69°	σ^2,π
[$W(CH_2C_6H_4CH_2)_3$]	79°	σ^2,π
[$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$]	88°	σ^2,π - π^2
[$Co(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)$]	96°	π^2
[$Fe(CH_2CHCHCH_2)(CO)_3$]	97°	π^2
[$Co_2(CH_2CHCHCH_2)(CO)(\eta^5\text{-}C_5H_5)_2$]	108°	π^2

Figure 1.52

With increasing contribution of metal - π - ligand interaction however we would expect the fold angle to increase ; and at the π^2 extreme the metal should be situated directly below the plane C(1)C(2)C(3)C(4) with the metal to carbon distances approximately

equal and with the fold angle $\Phi > 90^{o}$ ($\Phi \sim 115^{o}$) , (figure 1.53).



Tetrahapto - coordination

Figure 1.53

A table of fold angles , calculated from the crystal structures using a CHEMX molecular graphics package , is presented together with bonding assignments , (figure 1.52).
The variation of fold angles , as observed , would not only seem to give an indication of the type of metal - ligand interaction , but offer a direct correlation between the two.

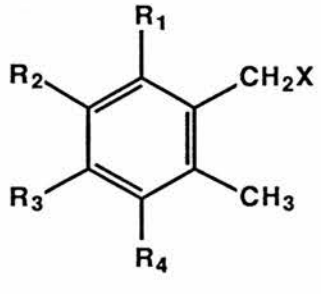
CHAPTER TWO

O-QUINODIMETHANE COMPLEXES OF RUTHENIUM(0)

2.1 Introduction

In chapter one it was shown that o-xylidene complexes of ruthenium can be prepared by reaction of the Grignard reagent, o-methylbenzyl magnesium bromide, and suitable ruthenium precursors. The reaction is reasoned to occur via a δ-hydrogen abstraction process seen previously in the loss of methane from methyl(naphthylmethyl)bis(triphenylphosphine)platinum(II) [55], and in the loss of o-xylene from [cis - $Pt(PEt_3)_2(CH_2C_6H_4CH_3)_2$] [37].

While the reaction appears relatively simple, further development and extension of the synthesis is limited greatly by the fact that the organic precursors required, of the type (**63**), (figure 2.1), are not readily available.



X = Cl or Br

(63)

Figure 2.1

This chapter will discuss the use of organolithium reagents as an alternative to the Grignard reagents, explaining the advantages,

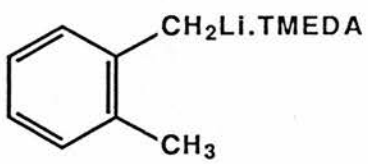
disadvantages and improvements that can be made in the synthesis. Included will be a comprehensive interpretation of the ^{1}H , ^{13}C , and ^{31}P n.m.r spectra of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] which will be related to the crystal structure obtained for the analogous compound [$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$]. An extension of the synthesis , to prepare methyl substituted o-xylidene complexes of ruthenium , via the organolithium method will also be described. The chapter will conclude with an analysis of the effect different phosphine / phosphite groups have on the reaction mechanism , and on the nature of the products.

2.2 Lithiation of o-xylene

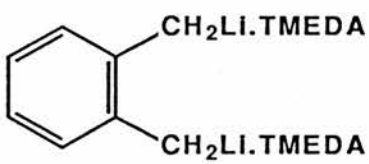
In general unactivated saturated hydrocarbons are inert to metallation and have tended to be used as solvents [56]. Benzene is only slightly metallated by butyl lithium in ether [57,58]. Toluene is also very difficult to metallate by the usual organolithium reagents [59]. The use of lithiating agents of the type alkyl lithium - amine , however , adds an extra dimension to their use. Butyl lithium -TMEDA metallates toluene to give benzyl lithium -TMEDA quantitatively within 1 hour , a clear example of the significant rate enhancement afforded by the presence of the amine [60]. In addition we see a high degree of regioselectivity , in many cases the often undesired ring metallated products are not produced. The function of the TMEDA is thought to be the

depolymerization of the hexameric n-butyl lithium to the kinetically more reactive monomer via coordination of the nitrogen atoms of the bidentate ligand with the lithium atom.

It has been reported that metallation of o-xylene [61] with a four-fold excess of BuLi -TMEDA produces the monolithiated species , (**64** , 49%) and the dilithiated species , (**65** , 51%) , (figure 2.2).



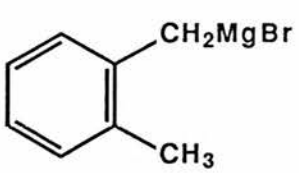
(64)



(65)

Figure 2.2

It is reasonable to assume therefore that a 1 : 1 ratio of o-xylene and BuLi -TMEDA should produce predominantly the monolithiated species.



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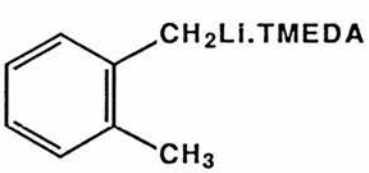


(64)

Figure 2.3

A comparison of the monolithiated derivative of o-xylene with o-methylbenzyl magnesium bromide , (**66**) , (figure 2.3) , suggests that it should be a viable alternative in the synthesis of o-xylidenes of ruthenium , and that significantly therefore the requirement for the organic precursor is now that we have methyl groups ortho to one another on the aromatic ring , a situation which is commonly found. Similarities with the di-Grignard reagents used by Lappert and Dixneuf , suggest that any dilithiated derivative which may be formed should also react to produce the required product. Important also , is that ring metallation , which cannot form the desired product , is only observed with a BuLi -TMEDA ratio of 4 : 1 , (a ratio of 1 : 1 is usually used) , and is therefore unlikely to occur to any significant extent.

The obvious advantage of using the organolithium reagent as we have already stressed is that of the ready availability of the organic precursor , in this case , o-xylene. It has a disadvantage in that while the concentration of Grignard solutions can be determined by a simple acid-base titration , the procedure is more complicated for organolithium - amine reagents.

2.3 Determination of alkyl lithium - amine concentration

The necessity for a reliable analytical procedure to determine the organolithium concentration in a solution is obvious.

There have been numerous studies [62-74] aimed at developing such a procedure. The most commonly used method of analysis has been a double titration in which benzyl chloride is used to destroy the RLi compound [64]. Subsequent results however showed that benzyl chloride does not react quantitatively with RLi to give non-basic products and consequently low concentration values are obtained. 1,2-dibromoethane has now been found to give a satisfactory analysis and has been recommended for general use [75].

The double titration method is as follows :-

The first acid-base titration requires for the alkyl lithium to be converted to LiOH by hydrolysis. Titration with acid then gives the total concentration (X) of base present in solution , according to the equation (figure 2.4).

$$aRLi + bROLi + cLiOH + dLi_2O \xrightarrow{H_2O}$$

$$(a+b+c)LiOH + dLi_2O + aRH + bROH$$

$$(X)$$

Figure 2.4

The second acid-base titration requires that the alkyl lithium be destroyed by reaction with 1,2-dibromoethane. Hydrolysis and titration with acid yields the concentration of base present in the

solution (Y) , which is not due to the alkyl lithium , according to the equation (figure 2.5) . A simple subtraction gives the concentration of the alkyl lithium.

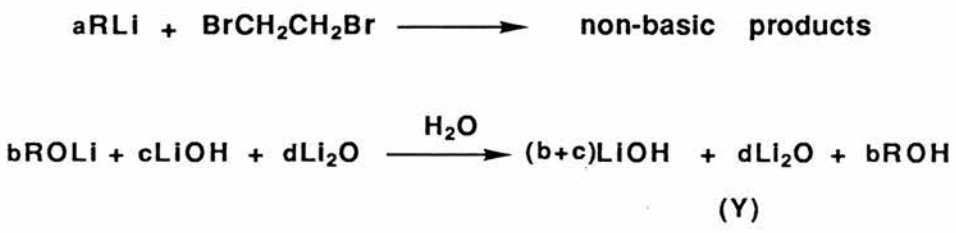


Figure 2.5

The procedure is somewhat complicated when one attempts to determine the concentration of alkyl lithium -TMEDA present in a solution. TMEDA itself is a base and account of this must be made in the analysis.

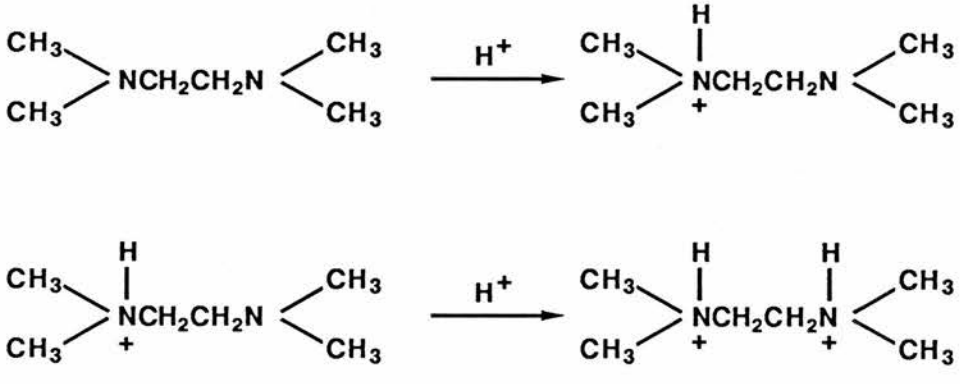
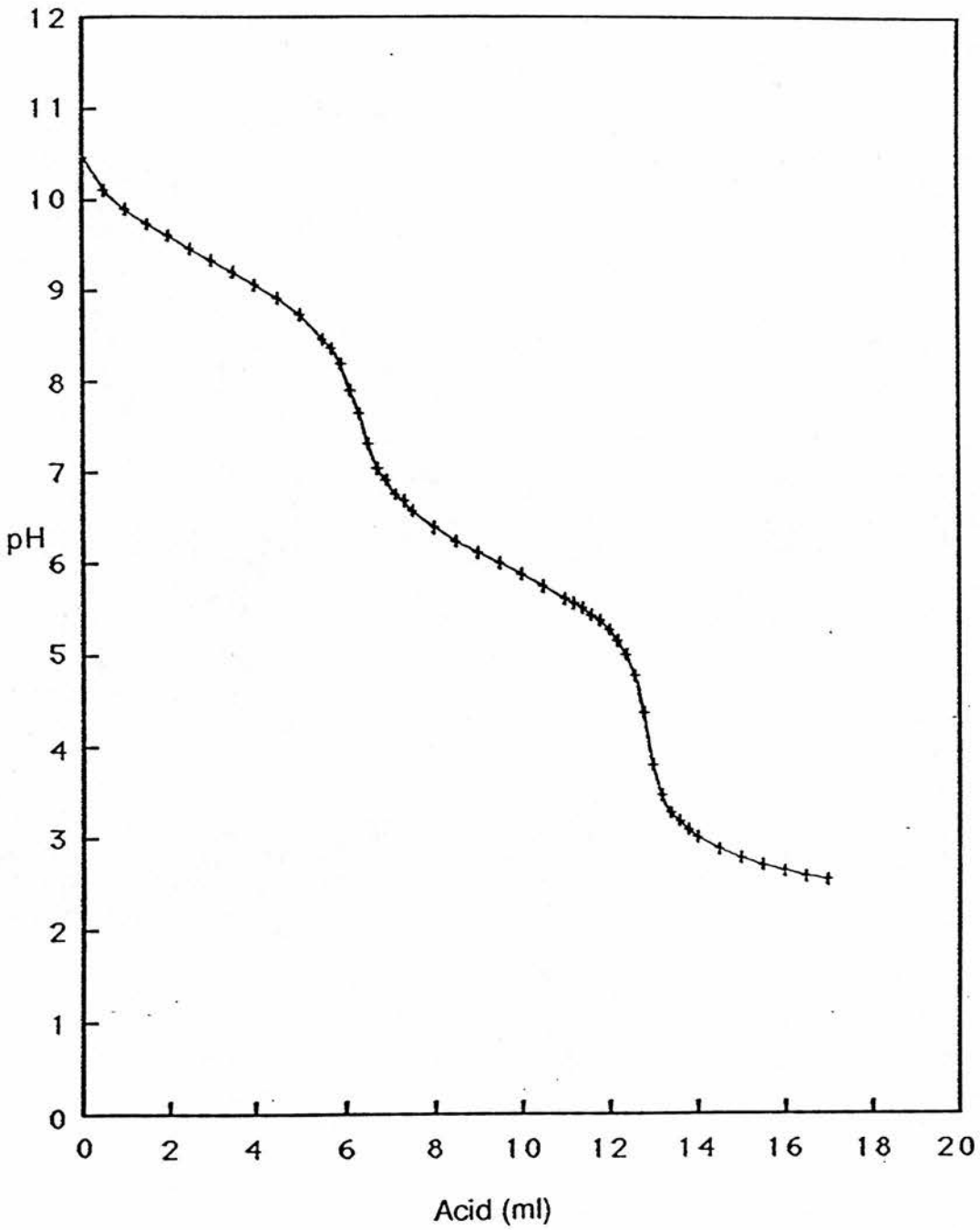


Figure 2.7

Titration of TMEDA produces two points of inflection , (plot of



Titration of TMEDA pH versus 0.1 N HCl

Figure 2.6

pH versus volume of added acid) , as expected for a dibasic compound , (figure 2.6) , the end points occurring over the pH ranges 8.5 - 6.5 and 5.5 - 3.0 and corresponding to the following reactions , (figure 2.7).

Titration of a reaction mixture consisting predominantly of LiOH and TMEDA would be expected to produce three points of inflection , the first due to the neutralization of the strong base LiOH , and the second and third due to the protonation of the TMEDA as described previously. This is indeed precisely what is observed , a point of inflection (pH range 12 - 10) , due to the neutralization of the LiOH , and two points of inflection , over the expected ranges for the TMEDA , (figure 2.8).

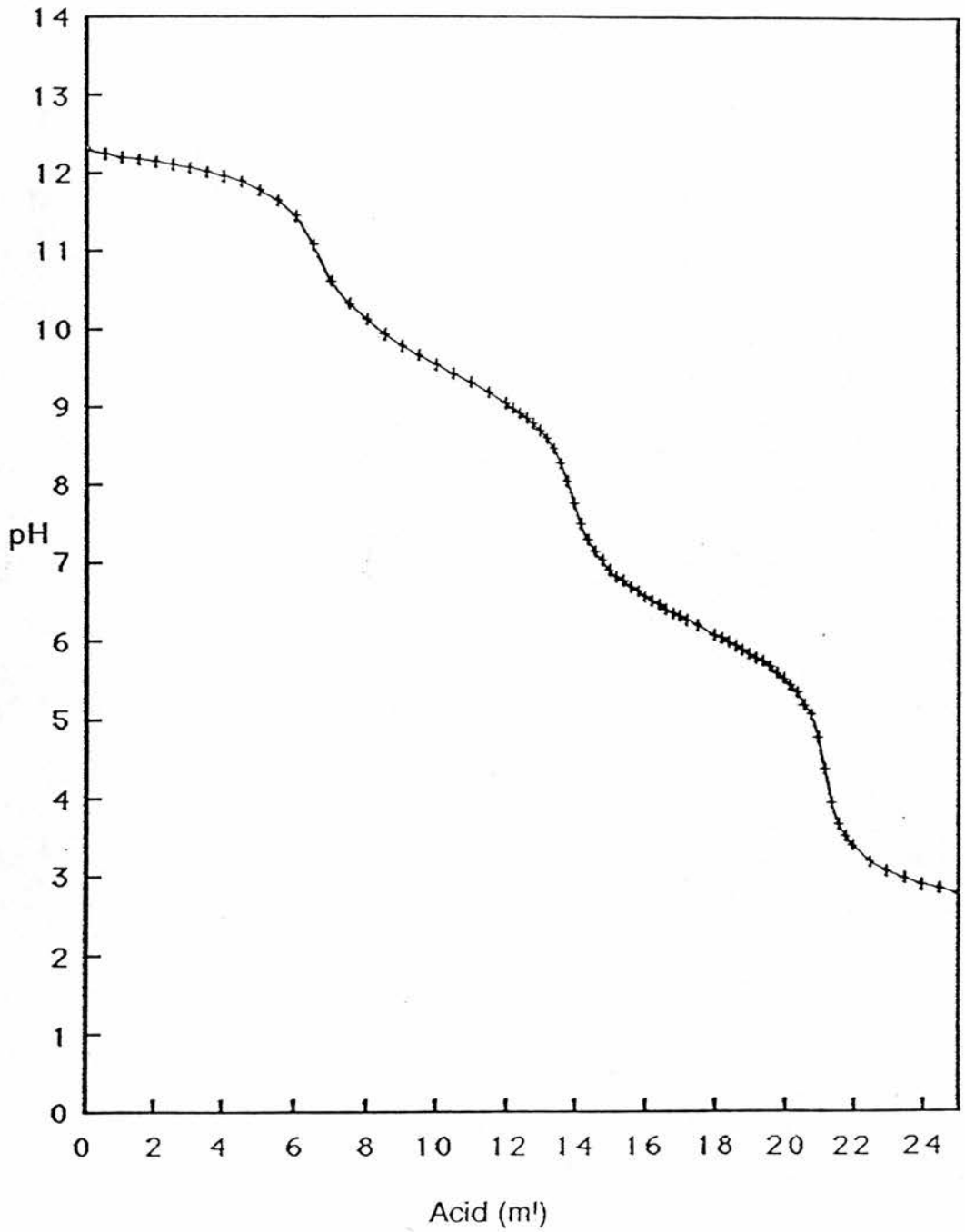
From the above description , it is clear that a double titration procedure should still be sufficient to calculate the concentration of alkyl lithium -TMEDA in a solution. The only observable difference will be the amount of acid required and the pH of the end-point.

$$aRLi.TMEDA + bROLi + cLiOH + dLi_2O \xrightarrow{H_2O}$$

$$(a+b+c)LiOH + dLi_2O + aRH + aTMEDA + bROH$$

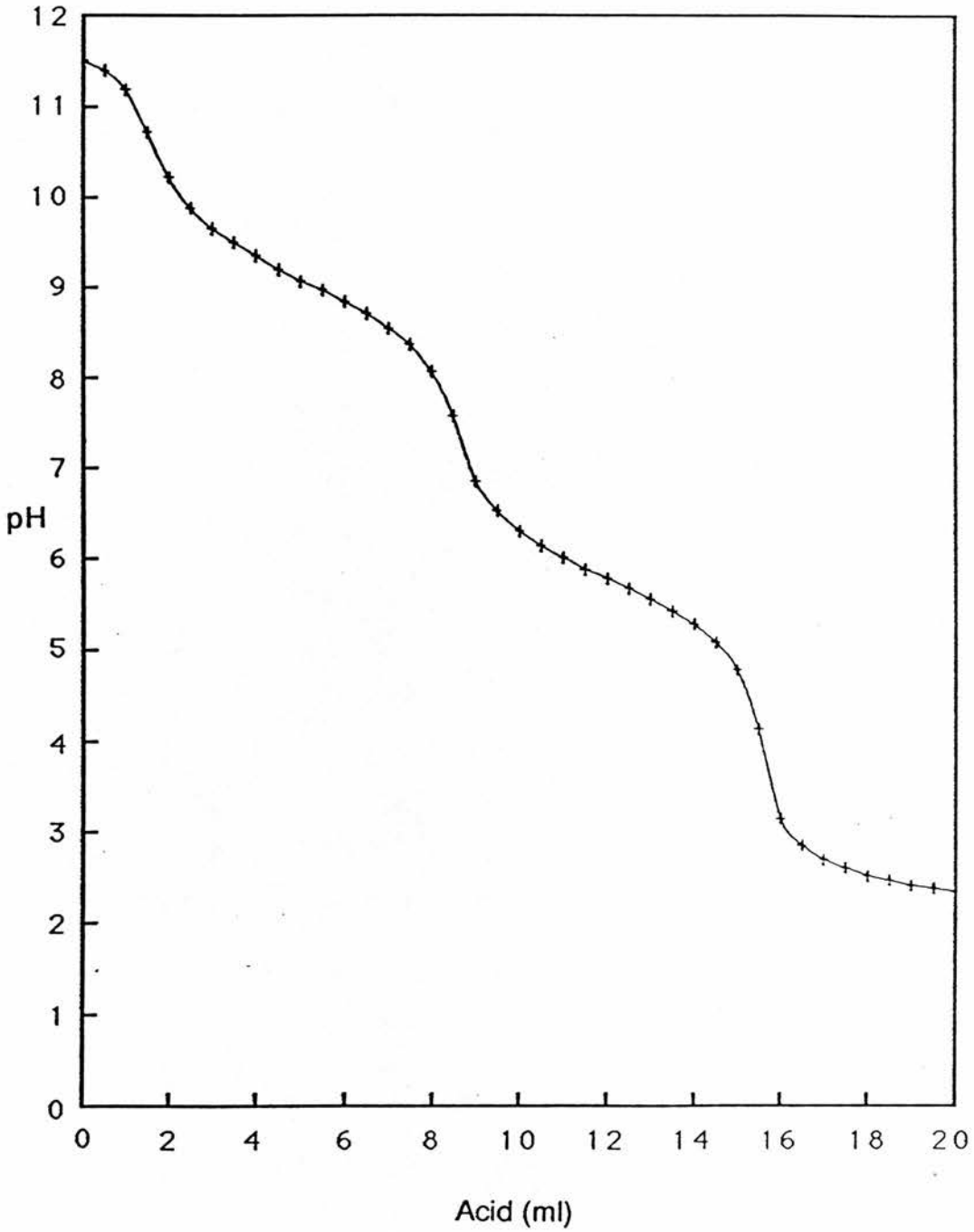
(X)

Figure 2.9



Titration of a hydrolyzed solution of
1-lithiomethyl-2-methylbenzene.TMEDA
pH versus 0.1 N HCl

Figure 2.8



Titration of a hydrolyzed solution of
1-lithiomethyl-2-methylbenzene.TMEDA
(previously reacted with dibromoethane)
pH versus 0.1 N HCl

Figure 2.10

The first acid-base titration again measures the total concentration of bases present. It requires for the alkyl lithium -TMEDA to be hydrolyzed. Titration with acid gives the total concentration of base present , (X) , according to the equation , (figure 2.9).

The second acid-base titration requires that the alkyl lithium -TMEDA be destroyed by reaction with 1,2-dibromoethane. Hydrolysis and titration , (figure 2.10) , with acid yields the concentration of base present in the solution which is not due to the alkyl lithium , (Y) according to the equation , (figure 2.11).

$$aRLi.TMEDA + BrCH_2CH_2Br \longrightarrow \text{non-basic products} + aTMEDA$$

$$aTMEDA + bROLi + cLiOH + dLi_2O \xrightarrow{H_2O}$$

$$(b+c)LiOH + dLi_2O + bROH + aTMEDA$$

$$(Y)$$

Figure 2.11

Again a simple subtraction provides the concentration of alkyl lithium-TMEDA.

2.4 Preparation of [$Ru(CH_2C_6H_4CH_2)P_3$]

Reaction of [$RuCl_2P_4$] , (P=PMe_3 , or PPh_2Me) , with two or more mole equivalents of 1-lithiomethyl-2-methylbenzene.TMEDA

at room temperature in diethyl ether leads to compounds analyzing as [$Ru(CH_2C_6H_4CH_2)P_3$] and having spectral characteristics entirely consistent with those obtained for the o-xylidene complexes using the o-methylbenzyl magnesium bromide Grignard reagent [43].

Reaction of [$RuCl_2P_4$] with only one mole equivalent of organolithium reagent leads to [$Ru(CH_2C_6H_4CH_2)P_3$] and unreacted [$RuCl_2P_4$].

There are a number of experimental problems common to both synthetic routes.

The metal halides , lithium chloride , magnesium chloride and magnesium bromide , produced as a result of the reactions have a tendency to remain in solution , (particularly in solvents such as diethyl ether , tetrahydrofuran and toluene). The more normal , and time consuming procedure for removing these is repeated concentration and filtration of the solution until no more precipitate is observed. Column chromatography was experimented with as an alternative , using the commonly available stationary phases , silica , alumina and florisil , with a range of activities , and even experimenting at temperatures as low as -30°C. Although flash chromatography using a low activity stationary phase did appear to be successful in removing the metal halides a significant quantity of product was lost on the column. It was eventually found that addition of water , which

surprisingly had no detrimental effect on the o-xylidene , to the ethereal reaction mixture dissolved the metal halides. A simple separation of the two solvent layers and drying of the ethereal layer containing the complex produced the most successful results.

As a result of the requirement of the reaction for two mole equivalents of the organolithium reagent , a by-product of the reaction is one mole equivalent of the organic precursor , o-xylene. While not a problem in this instance , o-xylene (bp 140°C) is easily removed by evaporation at room temperature in vacuo , one can envisage a problem when using precursors with much higher boiling points which cannot be removed so easily.

To this aim a simple sublimation process was employed , requiring heating of the complex mixture in vacuo until the organics were seen to deposit on a cold-finger probe inserted into the reaction vessel. The probe could be removed , cleaned , and re-inserted and the process continued until all unwanted materials had been removed.

Another consequence of the reaction is the release of one mole equivalent of phosphine. The phosphines initially used , namely , methyldiphenylphosphine , (PPh_2Me , bp 120°C / 1.5mm) , and dimethylphenylphosphine , (PMe_2Ph , bp 75°C / 12mm) , have very high boiling points and must be removed by the sublimation approach. Although the o-xylidene complexes are quite thermally robust some decomposition was observed due to the high temperatures required to remove these phosphines , use of a

lower boiling phosphine would obviously therefore be much more satisfactory.

Simple crystallization was difficult because of the very high solubility of the products in even traces of organic substrate or released phosphine.

It is interesting to note here, that while [$RuCl_2(PMe_3)_4$] does not react with o-methylbenzyl magnesium bromide even on warming, [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$], can be prepared using the organolithium route. Trimethylphosphine, (PMe_3, bp 40°C), has a very low boiling point and is easily removed by evaporation in vacuo, and is therefore a most suitable phosphine ligand.

With a satisfactory general procedure now available crystals of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] were prepared to enable a more detailed analysis of the spectral properties of these o-xylidene ruthenium complexes, and to relate these to the structure and bonding present.

[$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] was chosen for this purpose, primarily because of the relative simplicity of its spectra compared to those of [$Ru(CH_2C_6H_4CH_2)P_3$], ($P = PPh_2Me$ or PMe_2Ph). There are no phenyl resonances from the phosphine ligands to complicate the low field region of the ^1H n.m.r spectrum, allowing the observation of resonances from the ring hydrogens of the o-xylidene ligand. Similarly in the low field region of the ^{13}C n.m.r spectrum where only resonances due to

the ring carbons of the o-xylidene ligand are observed. The ^1H n.m.r high field region is also much easier to interpretate as the higher solubility of the trimethylphosphine complex allows a much higher concentration of complex in the sample and hence improved resolution , which is particularly important when analyzing the methylene hydrogens of the o-xylidene ligand.

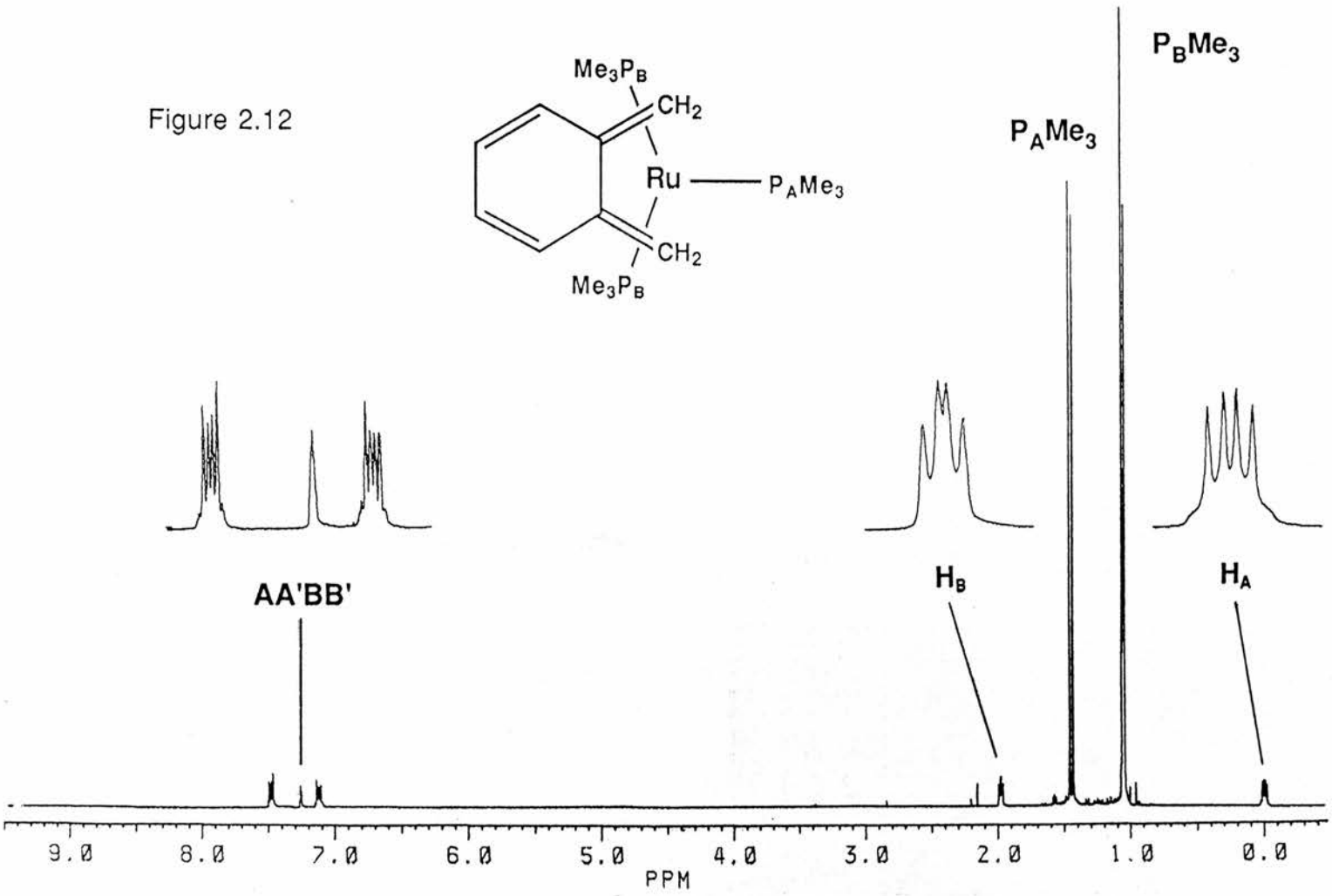
2.5 Spectral analysis of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$]

The art of high resolution nuclear magnetic resonance spectroscopy , (n.m.r) , has now become integral in the characterization of compounds both simple and complex. In recent years a bewildering array of specialized n.m.r techniques have been introduced capable of simplifying and solving hitherto unsolvable problems. A number of these were employed to solve the problems put forward by the spectra obtained for the ruthenium complexes.

2.5.1 ^1H n.m.r

The ^1H n.m.r spectrum of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] , (figure 2.12) , is very much as expected and is entirely consistent with

Figure 2.12



The ^{1}H n.m.r spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ (300 MHz) (C_6D_6, 25°C)

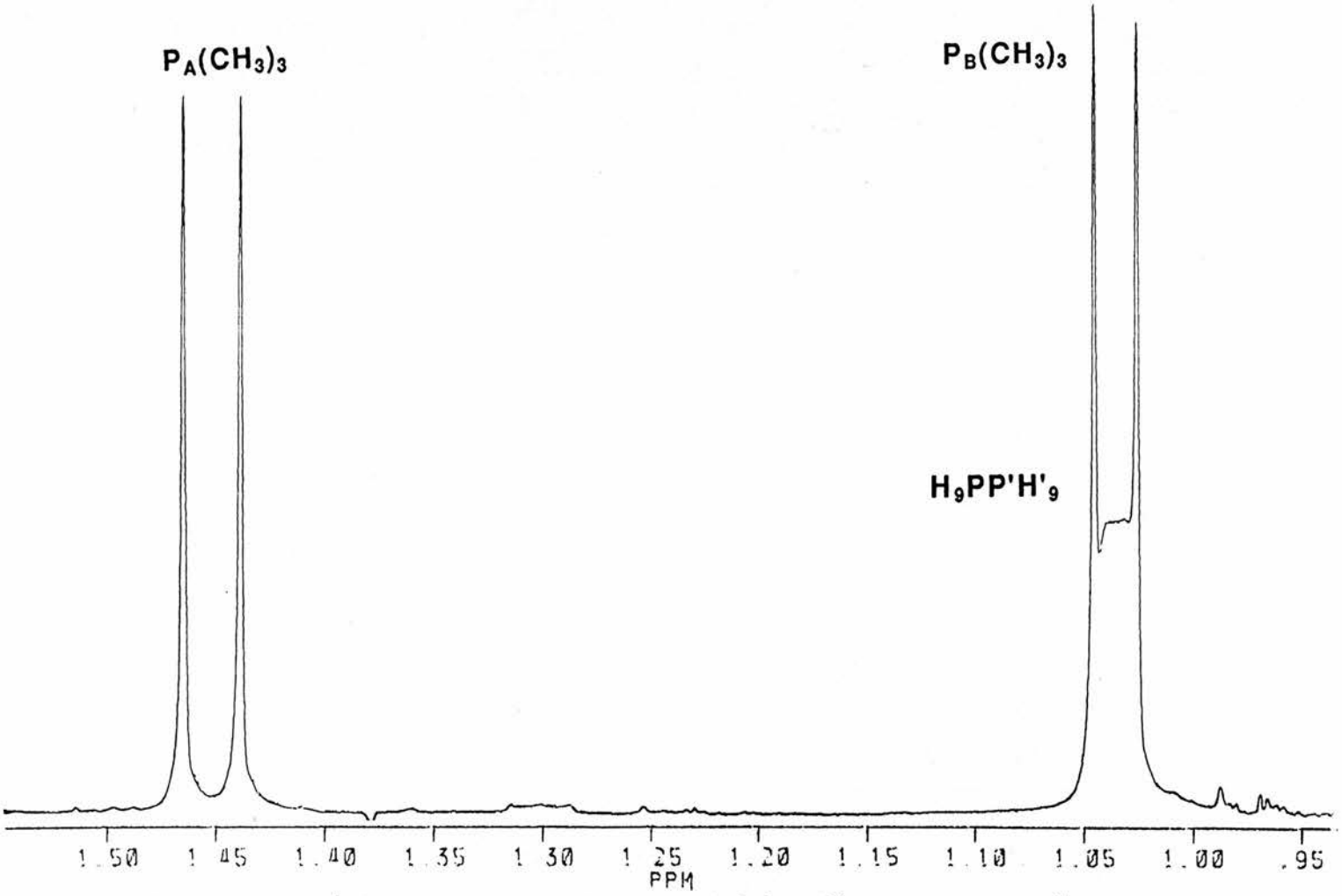


Figure 2.13 The ^1H n.m.r spectrum of the trimethylphosphine resonances of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ (300 MHz) (C_6D_6, 25°C)

these compounds retaining their solid state structure in solution. The familiar AA'BB'' pattern at low field confirms the plane of symmetry running through the center of the o-xylidene ligand, as seen in the X-ray structure of [$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$] [43]. Two signals are observed for the trimethylphosphine groups, (relative intensity 2 : 1). The methyl groups on the unique phosphorus atom, P_A, resonate as a doublet, ($^2J_{PH}$ = 7.92 Hz), whilst those on the equivalent phosphorus atoms, P_B, give a doublet with some intensity between the outer lines, ($^2J_{PH} + {}^4J_{PH'}$ = 5.87 Hz), a signal typical of an $A_nXX'A'_n$ spin system with $^2J_{PP}$ being small but non-zero [76], (figure 2.13).

The very different chemical shifts of the signals observed for the methylene groups of the o-xylidene ligand suggest two substantially different hydrogen environments. Each signal consists of a pseudo doublet of doublets. One can propose two possibilities to account for these observations.

Firstly that the methylene groups of the o-xylidene ligand are inequivalent. This approach explains the two environments, but fails to explain why they are so different, or the AA'BB' pattern in the low field region of the spectrum, a pattern which has already been suggested as confirming the symmetry of the ligand, but a symmetry which cannot be present if the methylene groups are inequivalent.

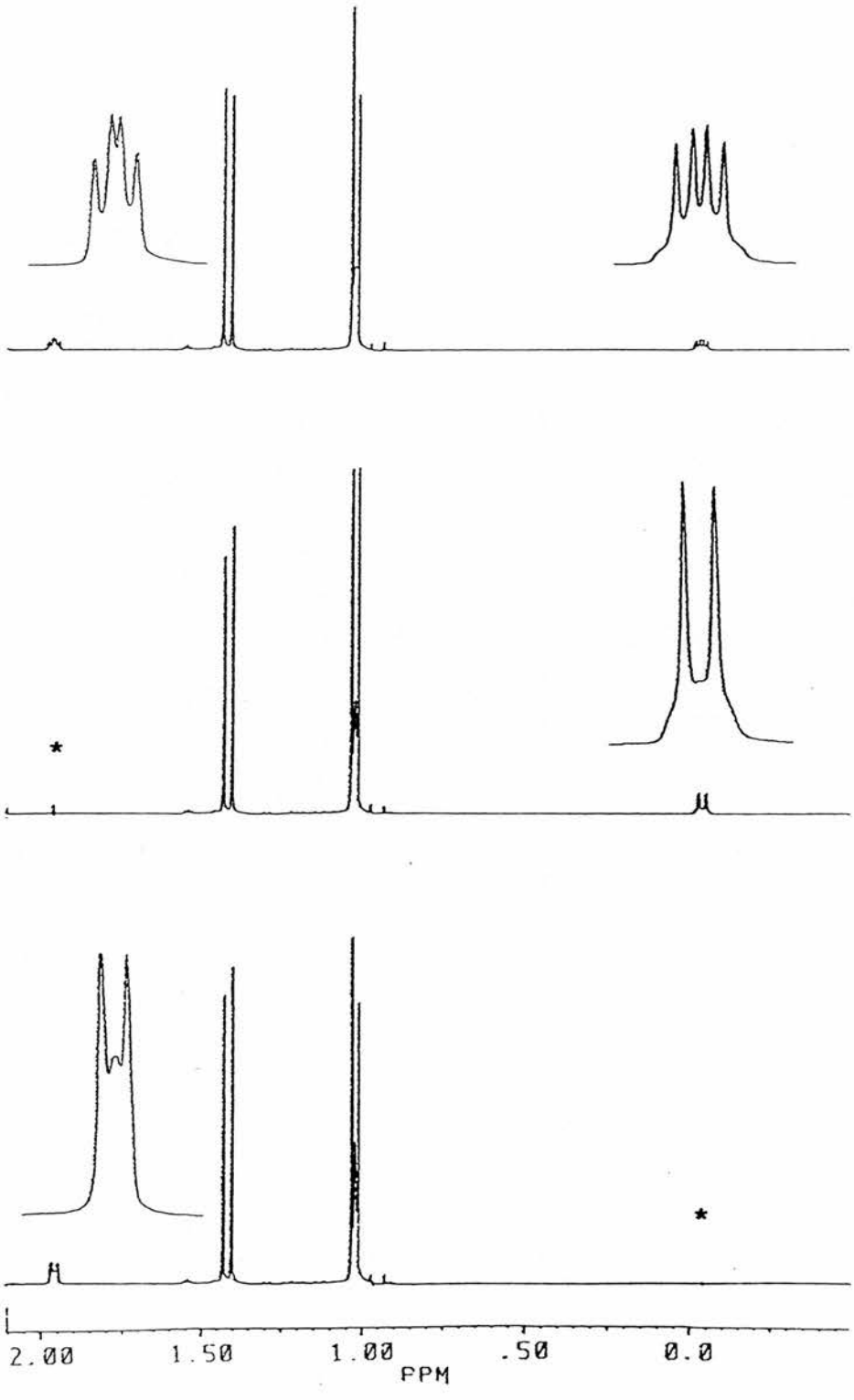
The second and more likely proposal, is that the methylene

groups are both equivalent , but that the hydrogens on each methylene carbon lie in very different environments. This would perhaps explain the large chemical shift difference between the two signals , and would also be consistent with the ligand having a plane of symmetry. This second situation is in fact not unusual and has been discussed in chapter one , particularly in reference to [$Fe(CH_2C_6H_4CH_2)(CO)_3$]. The two hydrogens on a particular methylene carbon should couple to one another. A simple series of homonuclear decoupling experiments confirm that this is the case.

2.5.2 Coherent Wave Decoupling

Coherent wave decoupling [77] involves the irradiation of one group of nuclear spins , X , with a monochromatic source of radiation , so as to modify the spin multiplet structure of any group of coupled spins , A. If the irradiation is centred on the chemical frequency of X and is sufficiently far away from the A resonance then the coupling between the two groups of spins is no longer observed in the spin structure of A. On the other hand if the irradiation is offset somewhat from this condition then the A spin multiplet splitting is scaled down , the apparent splitting increasing with decoupler offset and decreasing with the intensity of the radiation.

The experiment , (figure 2.14) , clearly shows coupling between



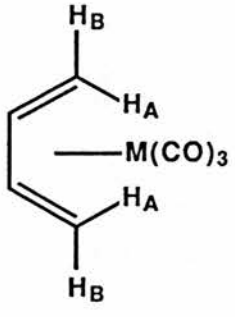
The ^1H n.m.r spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$
(300 MHz) (C_6D_6, 25°C)
(* denotes the position of the decoupler)

Figure 2.14

the two hydrogens H_A and H_B, ($^2J_{HH}$ = 3.72 Hz).

Zobl-Ruh and von Philipsborn [78] have carried out a structural comparison of (butadiene)tricarbonyliron, (butadiene)tricarbonylruthenium, and (butadiene)tricarbonylosmium based on computer simulation of ^1H and ^{13}C n.m.r spectra. They indicate that structural changes in the complexed ligand are reflected in the H,H-, C,H-, and C,C- coupling constants.

The geminal H,H- couplings, $^2J(H_AH_B)$, (figure 2.15), show a steady trend towards more negative values, which have to be compared with the value of +1.74 Hz in uncomplexed butadiene [79].



	$^2J(H_AH_B)$
Fe	- 2.42 Hz
Ru	- 2.77 Hz
Os	- 3.48 Hz

Figure 2.15

This effect has been ascribed [80] to a significant rehybridization towards sp^3 at the terminal carbon atoms. For comparison, the corresponding values in ethylene, (+ 2.5 Hz) [81], cyclopropane, (- 4.3 Hz) [82], and methane, (- 12.4 Hz) [83,84] may be consulted.

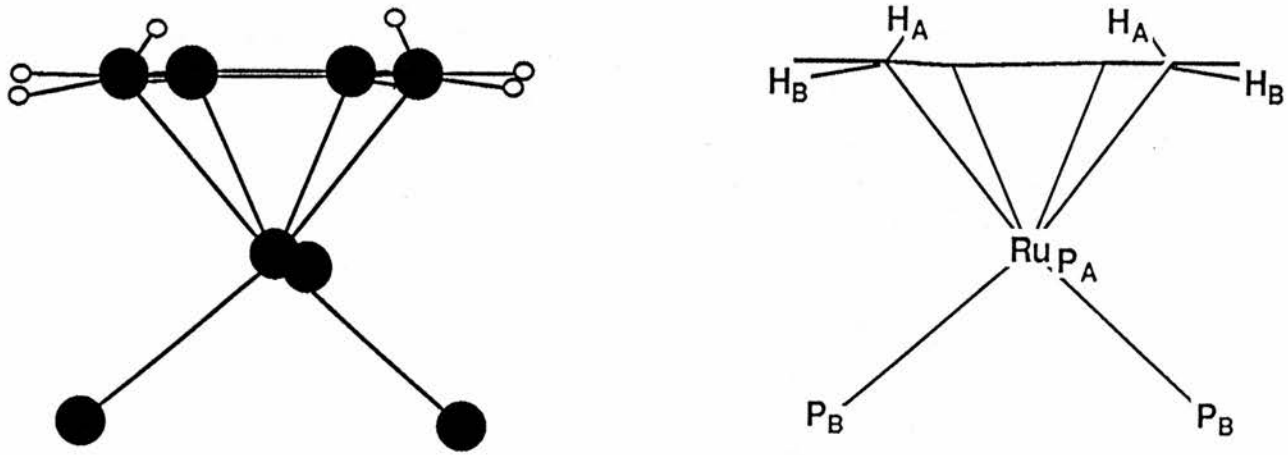
The value of 3.72 Hz obtained for the geminal H,H- coupling

in our o-xylidene ruthenium complex , and which now may presumably be assigned as - 3.72 Hz , would also seem , on this basis , to suggest a significant rehybridization towards sp^3 at the terminal carbon atoms of the ligand , and therefore create a non-planar ligand skeleton. As for the relative positions of the methylene hydrogens in the complex , Zobl-Ruh and von Philipsborn suggest for their compounds , on the basis of C,H-coupling constants , that the H_B hydrogens stay more or less in the ligand plane , whereas the H_A hydrogens are pushed away from the metal and out of the ligand plane. This would also seem to be in accord with Bergman's structural analysis of $[Co(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)]$ [44] , where he emphasizes the twisting observed for the methylene groups and locates the hydrogens accordingly.

An approximation of the relative positions of the methylene hydrogens has been added to the crystal structure models of $[Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3]$, (figures 2.16 , 2.17 and 2.18).

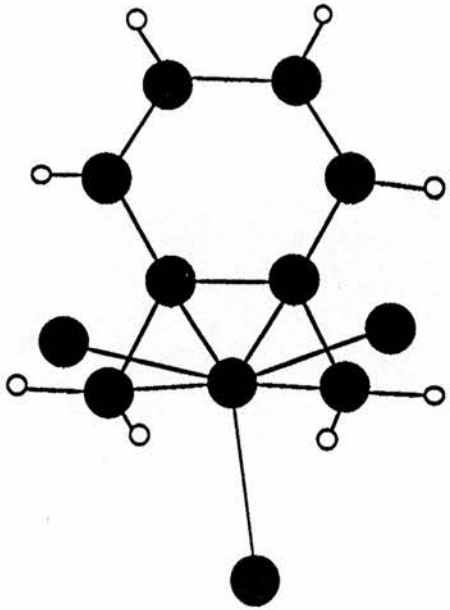
Although the value of J_{HH} allows the approximate positioning of the methylene hydrogens , the unusual high-field resonance of one set of these hydrogens remains to be explained.

The circulations of delocalized π-electrons generate magnetic fields that can either **shield** or **deshield** nearby hydrogens [85]. Whether shielding or deshielding occurs depends on the location of the hydrogen in the induced field. The deshielding of external



FRONT VIEW

Figure 2.16 CHEMX computer representation of the crystal structure of $[Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3]$



PLAN VIEW

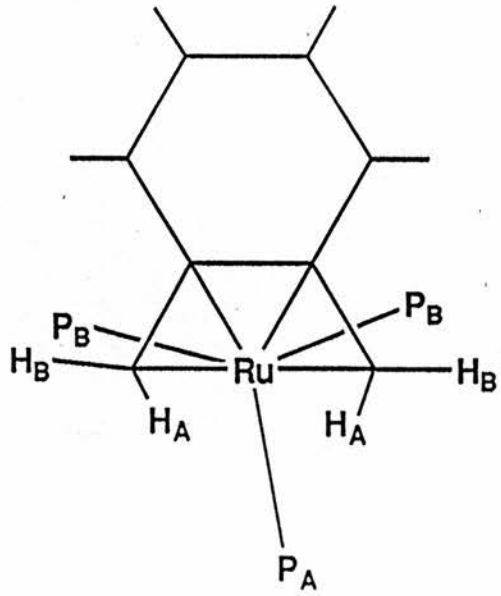
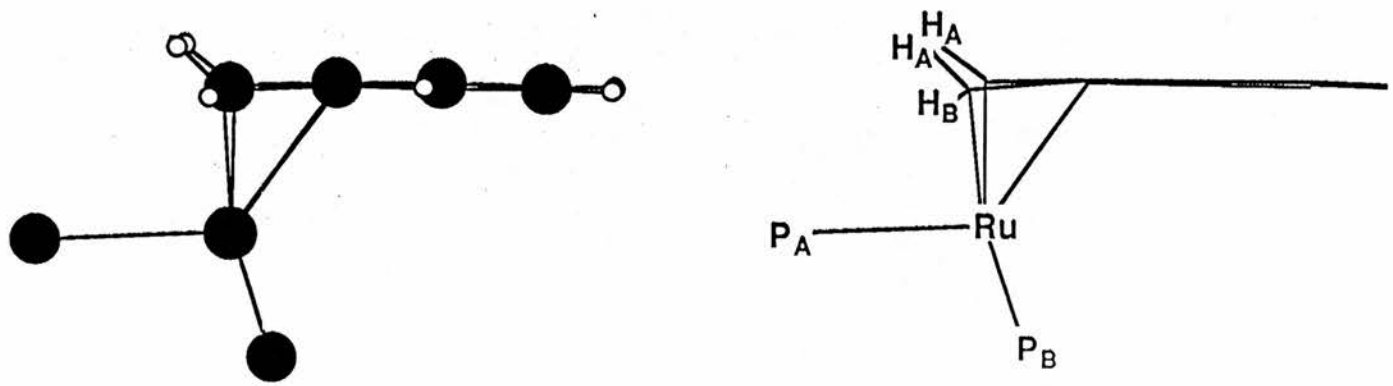


Figure 2.17 CHEMX computer representation of the crystal structure of $[Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3]$

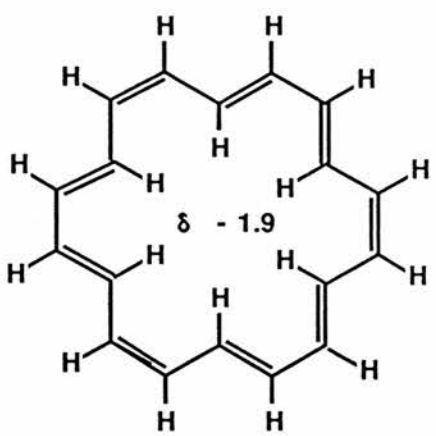


SIDE VIEW

Figure 2.18 CHEMX computer representation of the crystal structure of $[Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3]$

aromatic hydrogens that results from the circulating π-electrons is one of the best pieces of evidence chemists have for π-electron delocalization in aromatic rings. Not all aromatic hydrogens absorb at low magnetic field strengths , however . Large-ring aromatic compounds [86] have been synthesized that have hydrogens in the centre of the ring. These hydrogens absorb at unusually high magnetic field strengths , because they are shielded by the opposing induced field in the centre of the ring.

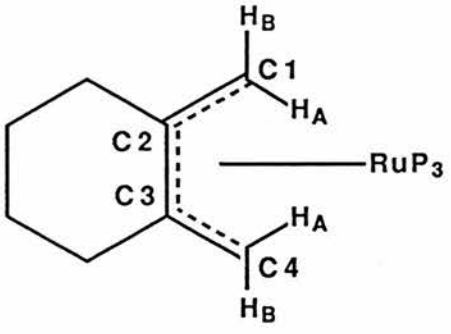
These internal hydrogens often absorb at field strengths greater than that used for the reference , TMS , δ 0 . The internal hydrogens of [18]-annulene , (**67**) , (figure 2.19) , absorb at δ - 1.9 [87,88].



(67)

Figure 2.19

By analogy , the presence of circulating π-electrons in the C1 , C2 ,



(68)

Figure 2.20

C3 , C4 fragment of the o-xylidene ligand , (**68**) , (figure 2.20) , would be expected to cause a similar (though obviously less effective) shielding of the internal H_A hydrogens , shifting them to high field.

This explanation would also seem to provide further confirmation of the intermediate π^2- , σ^2,π- , nature of the o-xylidene ligand in these complexes as discussed in chapter one.

Having ascertained that one of the couplings in the multiplets obtained for the methylene hydrogens , is due to a geminal H,H-coupling then the other major coupling in each case can be assigned as being a P,H- coupling. Quite clearly the shape of the multiplets also suggests that minor coupling to one or both of the remaining phosphorus atoms is occurring.

Using a technique called Resolution Enhancement the fine structure of these multiplets becomes discernible.

2.5.3 Resolution Enhancement

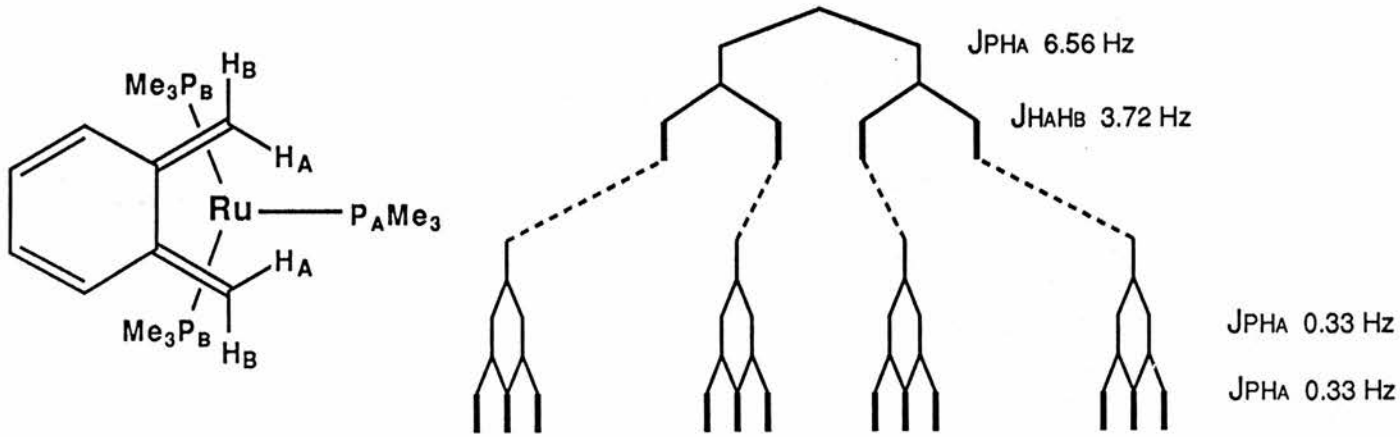
The most common approach to Resolution Enhancement is a mathematical treatment known as apodization [89], where either the signal-to-noise or the resolution can be improved.

Because the noise remains constant throughout the acquisition period but the signal decays, the early part of the FID contains a higher proportion of signal. Thus suppression of the later part of the FID relative to the early part will increase the apparent signal-to-noise ratio. Unfortunately this also has the added effect of broadening the lines.

The most useful resolution enhancement functions are those which bias the data against the early components to sharpen the lines and against the most long lived components to improve the signal-to-noise ratio.

The best function for enhancement of resolution with minimal loss of signal-to-noise is a Gaussian multiplication. This is a two-parameter function. The first parameter LB is a line broadening parameter, which when set negative will sharpen the signals. The second parameter GB determines the location as a fraction of the acquisition time where the function is at a maximum.

Using a Gaussian multiplication function as described, resolution enhancement of the ^{1}H n.m.r spectrum of



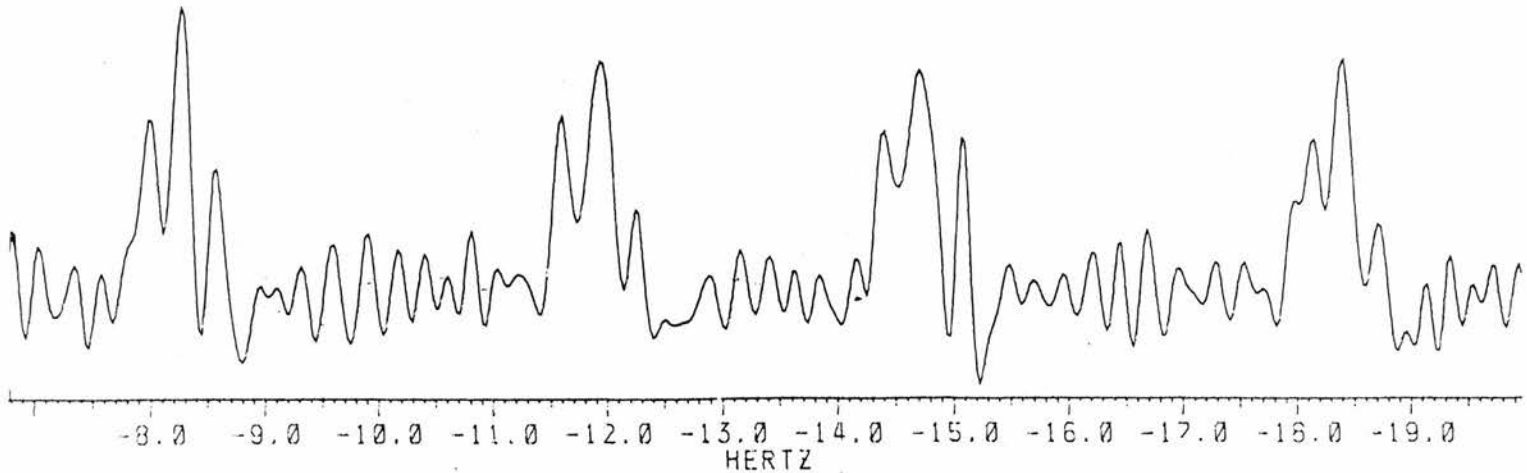


Figure 2.21 The Resolution Enhanced ^1H n.m.r spectrum of H_A

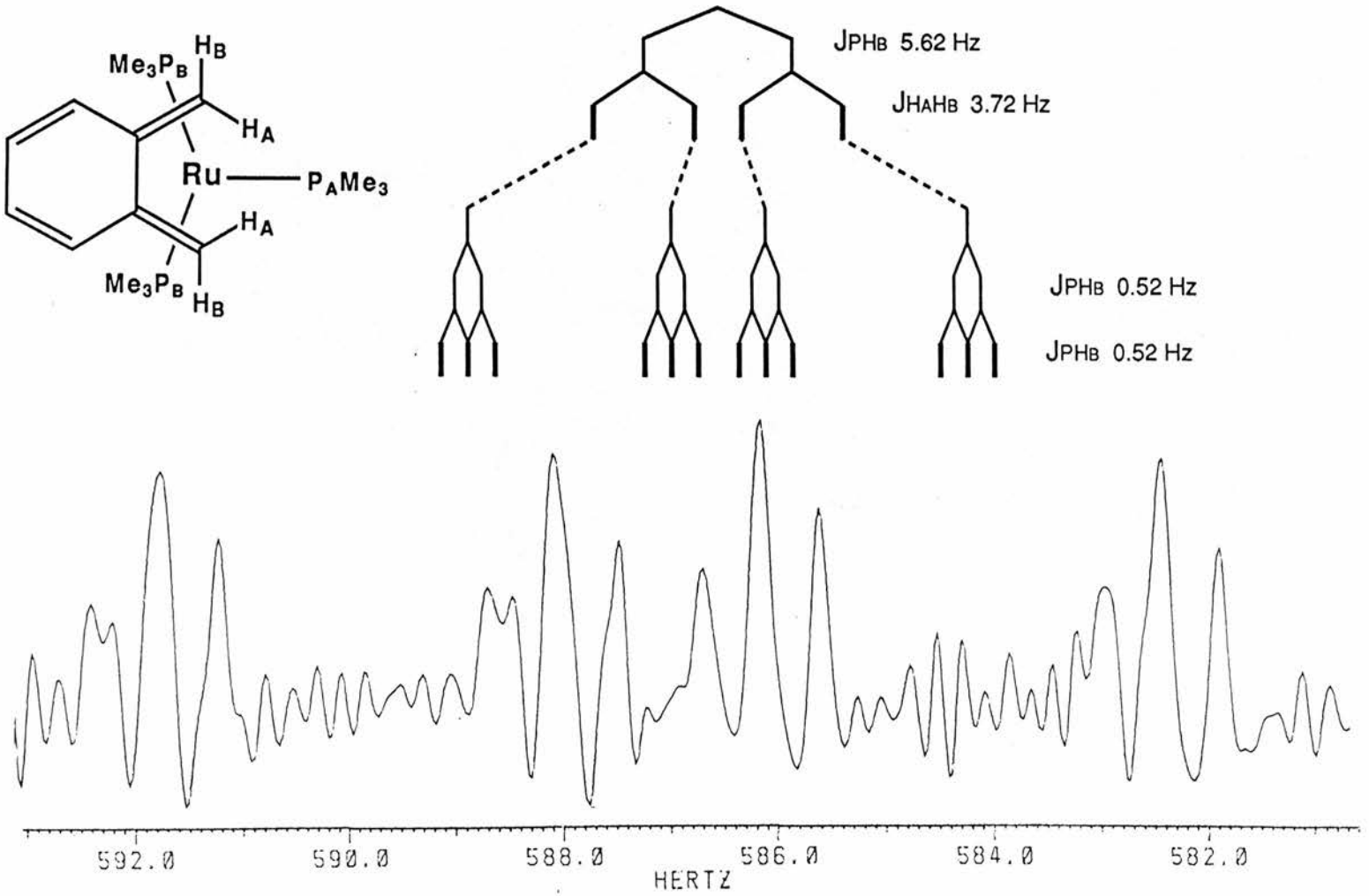


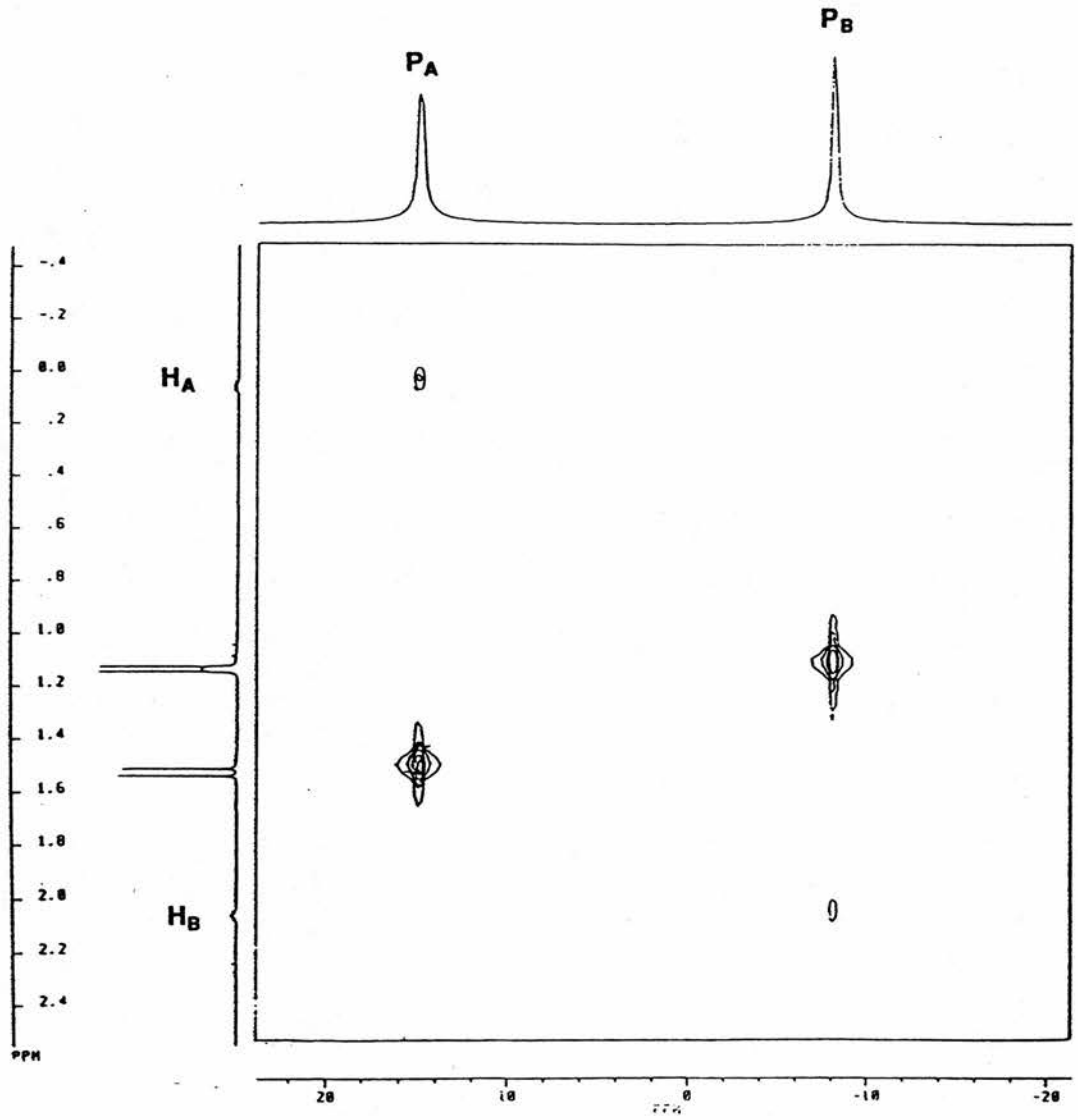
Figure 2.22 The Resolution Enhanced ^1H n.m.r spectrum of H_B

[$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] shows that the multiplets for the H_A, (figure 2.21), and H_B hydrogens , (figure 2.22) , rather than being described as pseudo doublets of doublets , can be better described as pseudo doublets of doublets of triplets. All the expected couplings are observed , and it is clear that each methylene hydrogen does in fact couple to all three phosphorus atoms in the complex. It is not clear however which particular phosphorus atom is coupling to which hydrogen .

2.5.4 Two dimensional NMR Spectroscopy

A multiple-pulse experiment contains preparation , evolution , and detection stages. The spectrum that is finally detected depends on the nature of the preparation and on the length of the evolution time. The evolution is not detected directly but may be ' mapped ' by carrying out many experiments with different evolution times. In this way two quite separate sets of spectroscopic features can be obtained i.e those that influence the magnetization during the evolution time and those that influence it during the acquisition time. Two - dimensional n.m.r uses a second Fourier transformation to convert the time dependence of the evolution into a second frequency easing the display and interpretation of the information.

A ^1H - ^{31}P correlation spectrum of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] , (figure 2.23) , obtained using a COLOC [90] sequence , because of



The ^{1}H - ^{31}P correlation spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$

Figure 2.23

the size of the couplings involved (normal 2D sequences require coupling constants of > 10 Hz), confirms the identification of the resonances due to the P_AMe_3 and P_BMe_3 groups in the ^1H n.m.r spectrum. More interestingly, it also shows that the major P,H- coupling to the H_A hydrogens is caused by interaction with the P_A phosphorus atom and the major P,H- coupling to the H_B hydrogens is caused by interaction with the P_B phosphorus atoms.

2.5.5 ^{31}P n.m.r

The ^{31}P n.m.r spectrum of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$], (figure 2.24), shows two resonances of approximate ratio 1 : 2, a triplet, (δ 14.87), and a doublet, (δ - 8.38). These clearly must be assigned to the unique, (P_A), and symmetry related, (P_B), phosphorus atoms respectively. There is coupling, ($^2J_{PP}$ = 8.72 Hz), between the two sets of atoms but it is relatively small. It should be noted that for these ruthenium complexes with P = PMe_2Ph or $PMePh_2$ the signals are singlets and no significant coupling is seen. Usual values for J_{PP} in five coordinate complexes of ruthenium (0) [91] or ruthenium (II) [92] are > 20 Hz. Very low couplings have been observed for other diene complexes of ruthenium [47,91], and zero couplings occur in [$Ru(C_4H_5R)(PPh_3)_2$(styrene)], (R = H or Et) [93]. These low

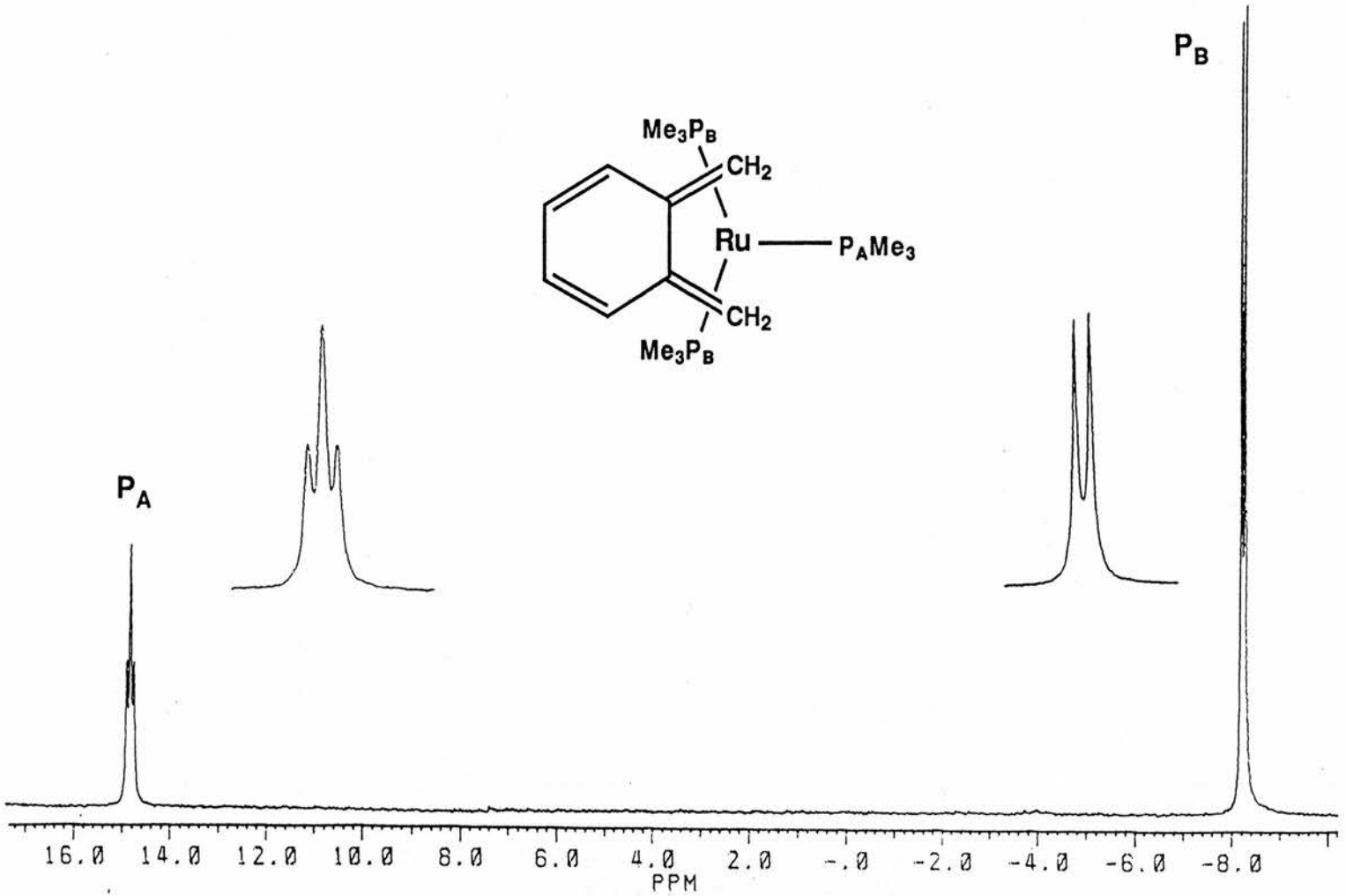


Figure 2.24 The ^{31}P-{^{1}H} n.m.r spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ (C_6D_6, 25°C)

couplings have been described as reflecting the P - Ru - P angles which for [$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$] will be close to the solid state value of 100° and probably similar to those found in tetrahedral complexes of nickel (0) for which J_{PP} is also zero [94]. In other five and six coordinate complexes of ruthenium (0), or ruthenium (II), angles of c.a. 90°, (octahedral, trigonal bipyramid, square pyramid), or 120°, (trigonal bipyramid), would be expected, and would give rise to the observed higher values of the coupling constants.

The lower steric requirements of the trimethylphosphine ligand on replacement of dimethylphenylphosphine in the o-xylidene complexes presumably allows for a change of the P - Ru - P angles thereby increasing the P,P- coupling somewhat.

2.5.6 ^{13}C n.m.r

The ^1H decoupled ^{13}C n.m.r spectrum, (figure 2.25), at first glance appears rather unexceptional. Closer inspection reveals a number of interesting features.

The three signals in the low field region of the spectrum, (δ 101.65, 122.97, 131.65), are attributable to the three sets of equivalent o-xylidene ring carbons. The signals at δ 122.97 and δ 131.65 can be assigned by their intensities to the C6,C7 and C5,C8 sets. These chemical shifts are comparable with those

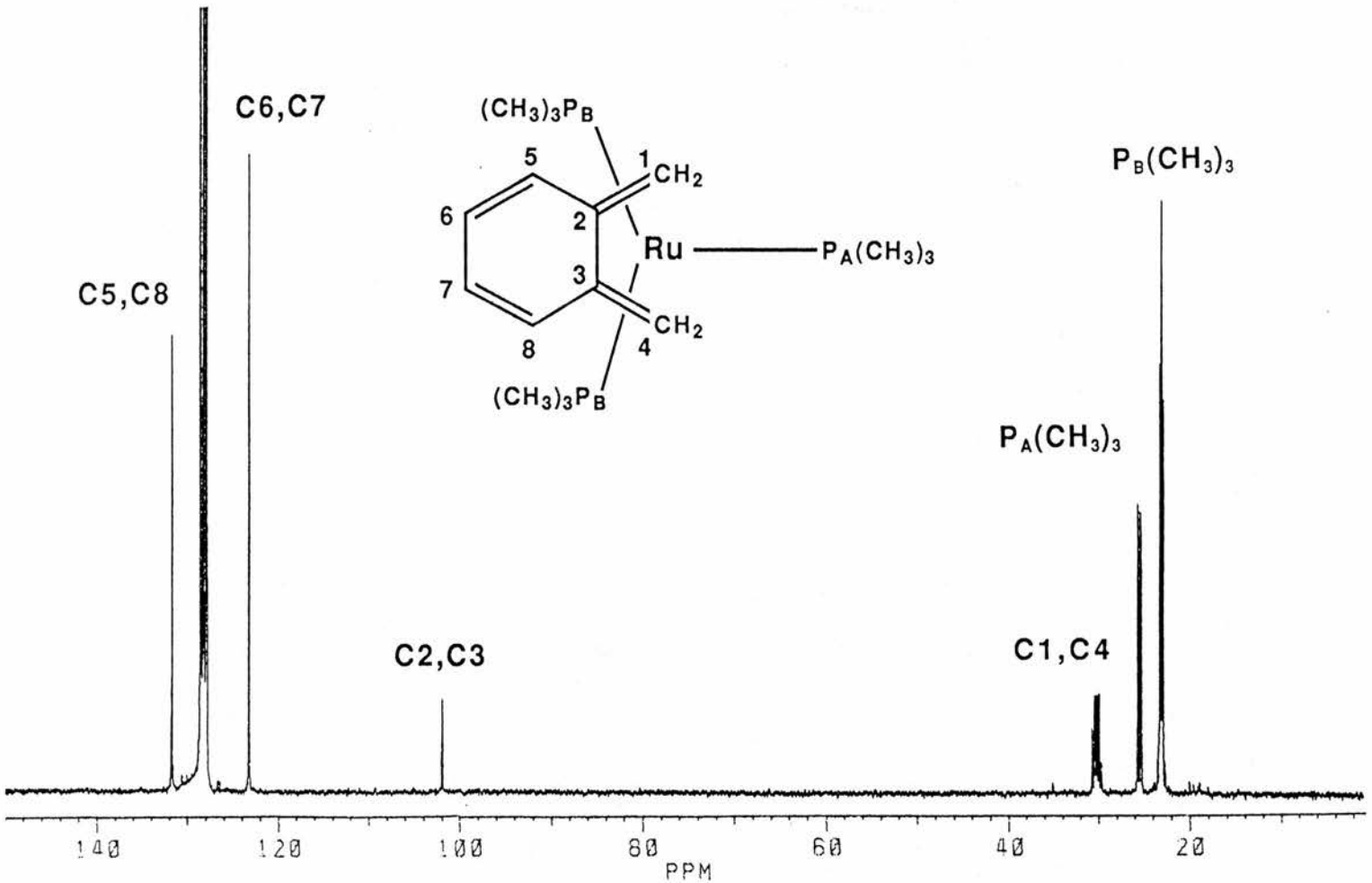


Figure 2.25 The ^{13}C-{^1H} n.m.r spectrum of $[Ru(CH_2C_6H_4CH_2)(PMe_3)_3]$ (C_6D_6, 25°C)

expected of carbons in a delocalized ring system.

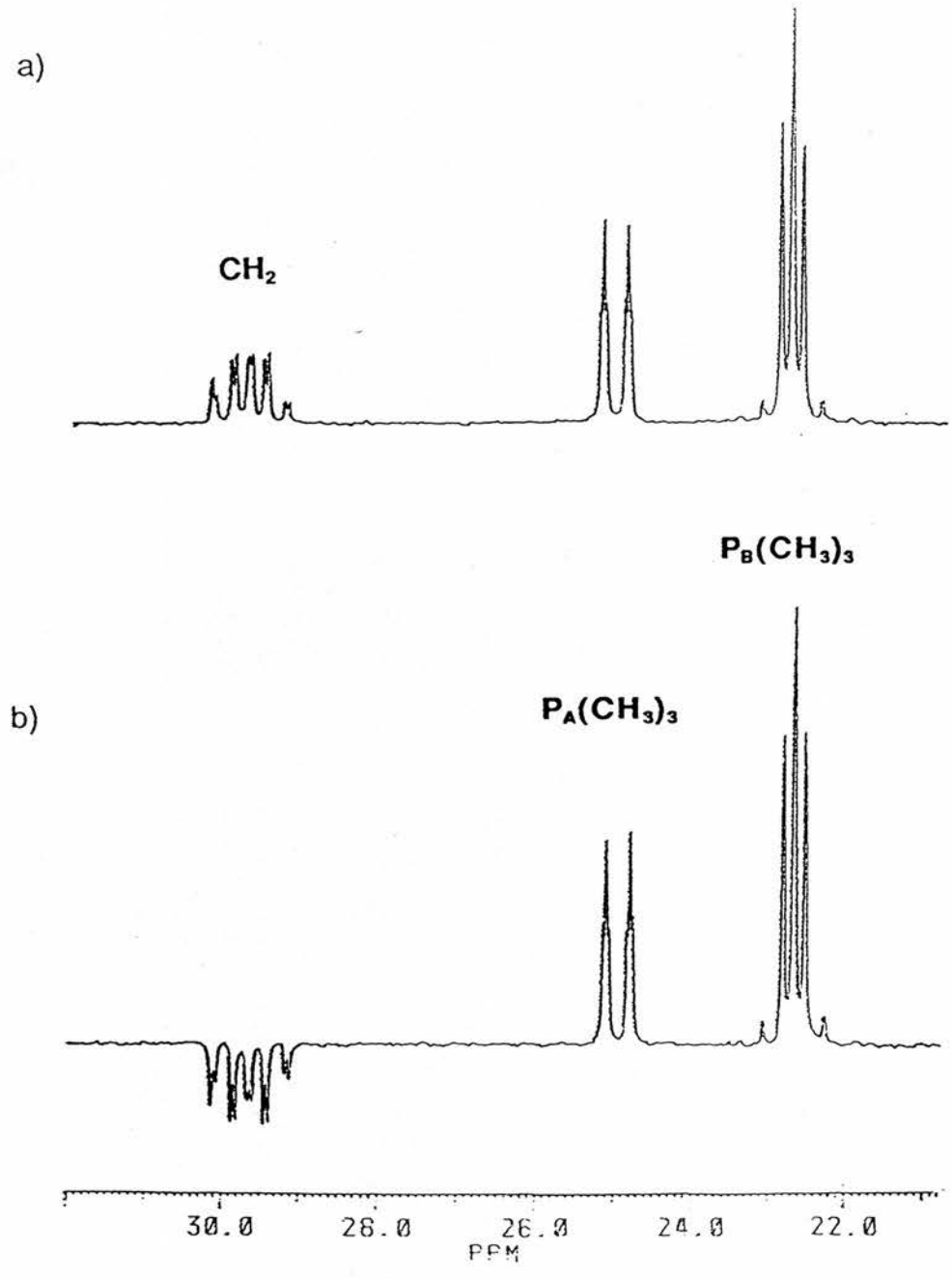
What is interesting to note is the remarkably different chemical shifts of the quaternary carbons , (C2,C3) , of the o-xylidene ligand , (δ 101.65). Comparison of this value with the values of the corresponding quaternary carbons of other o-xylidene complexes , (figure 2.26) , in which the bonding has been described as σ^2- , σ^2,π- , or π^2- , suggests that there is a direct correlation between the nature of the ligand-metal interaction and the chemical shift of the quaternary carbons , (C2,C3).

Complex	δC (ppm)	Bonding
[$Co(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)_2$]	92.1	π^2
[$W(CH_2C_6H_4CH_2)_3$]	116.9	σ^2,π
[$Zr(CH_2C_6H_4CH_2)(\eta^5\text{-}C_5H_5)_2$]	138.1	σ^2
[$Co_2(CH_2C_6H_4CH_2)(CO)_2(C_5H_5)_2$]	147.8	σ^2
[$Pt(CH_2C_6H_4CH_2)(PEt_3)_2$]	157.5	σ^2

Figure 2.26

Once again evidence would seem to suggest an intermediate σ^2,π- , π^2- bonding in the ruthenium o-xylidene complexes.

A preliminary inspection of the high field region of the spectrum suggests that the methylene carbons , (C1,C4) , of the



The High Field region of the
^{13}C-{^{1}H} n.m.r spectrum of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$]
a) Normal pulse sequence
b) DEPT-135 pulse sequence

Figure 2.27

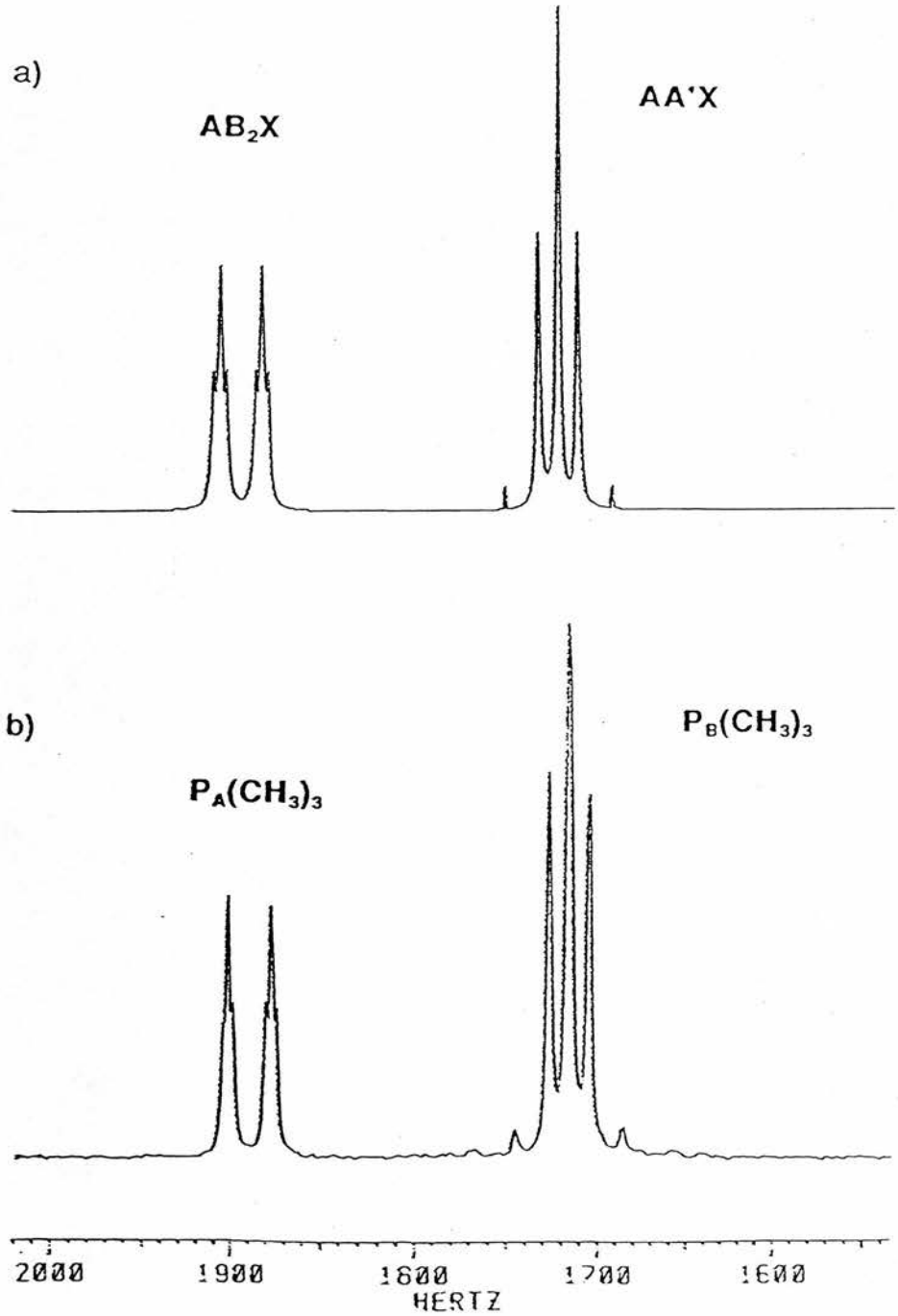
o-xylidene ligand resonate as a complex multiplet, (δ 29.70). This is confirmed by using a DEPT-135 pulse sequence which has the effect of inverting any carbons which are directly linked to two hydrogens, (figure 2.27). The methyl carbons of the unique phosphorus atom, (P_A) , resonate as a doublet of triplets, (δ 25.06), and the methyl carbons of the equivalent phosphorus atoms, (P_B), resonate as a multiplet characteristic of an AA'X pattern, (δ 22.76).

An explanation for the complex splitting patterns is as follows :-

The methyl carbons of the unique phosphorus atom, (P_A), are equivalent, (rotation about the Ru - P bond causes a time averaged situation), and couple to P_A , ($^1J_{PC} = 23.4$ Hz) to produce a doublet. Further smaller couplings, ($^3J_{PC} = 3.0$ Hz) to the two equivalent phosphorus atoms, (P_B), produces the observed doublet of triplets.

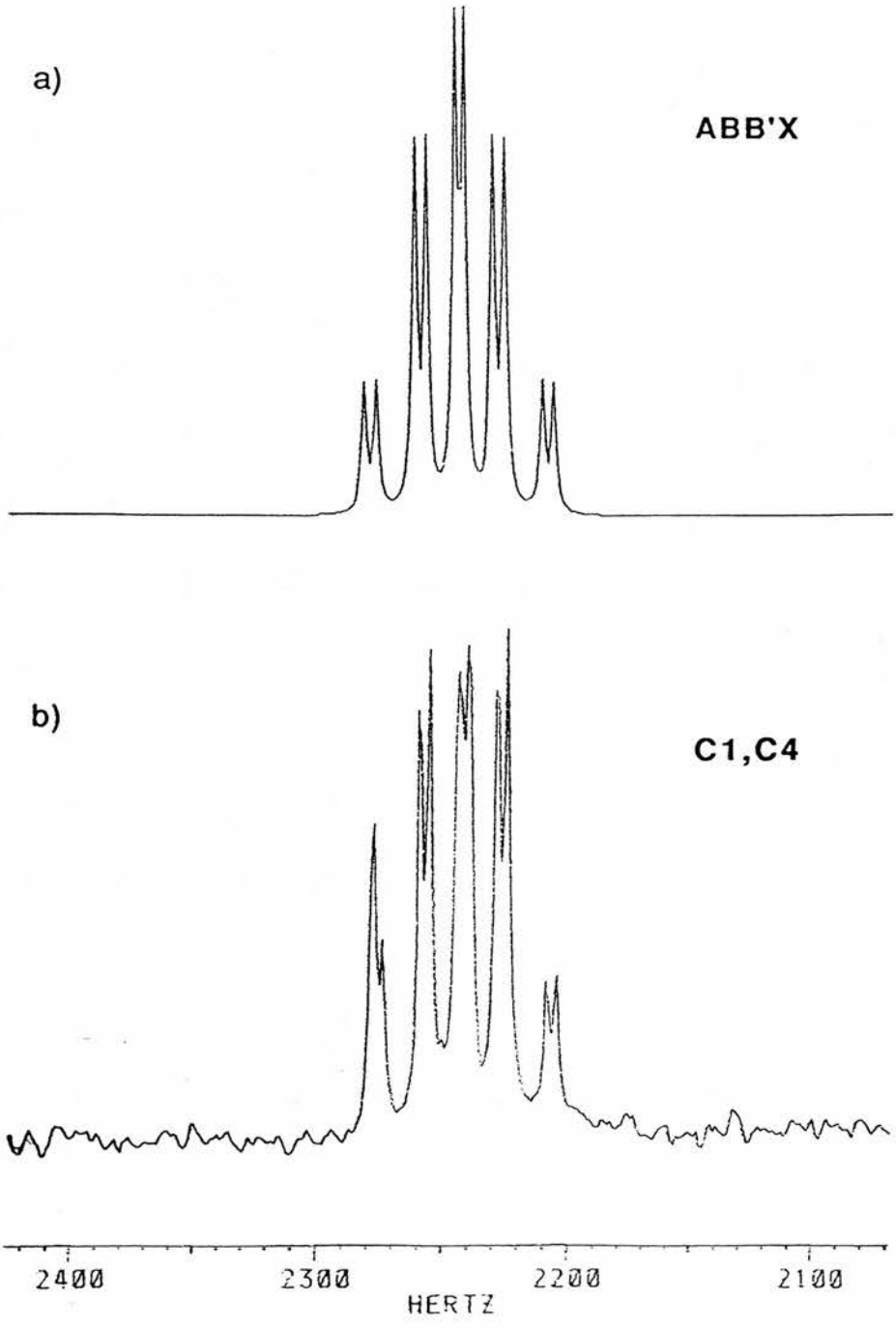
All the methyl carbons of the equivalent phosphorus atoms, (P_B), are equivalent. Coupling of the carbons to the directly adjacent P_B, ($^1J_{PC} = 19.95$ Hz), and further coupling to the other P_B, ($^3J_{PC} = 2.35$ Hz), produces the observed $P_BP_B'C$ spectrum , as confirmed by PANIC simulation, (figure 2.28).

A full analysis of the multiplet due to the methylene carbons is complex and can only be achieved by computer simulation. A PANIC programme is again used here, (figure 2.29). The results



^{13}C-{^{1}H} n.m.r spectra of the trimethylphosphine carbons
a) PANIC simulated spectrum
b) Experimental spectrum

Figure 2.28



^{13}C-{^{1}H} n.m.r spectra of the C1,C4 methylene carbons
a) PANIC simulated spectrum
b) Experimental spectrum

Figure 2.29

would seem to suggest a second order ABB'X pattern.

The coupling constants obtained can be explained by a further consideration of the 3-dimensional structure (figures 2.16 , 2.17 and 2.18).

The unique phosphorus atom , (P_A) , can be seen to couple equally to each of the C1 and C4 carbons , ($^2J_{PC} = 4.30$ Hz). Two further couplings are obtained. The very much larger , ($^2J_{PC} = 37.39$ Hz) , is attributed to the $P_{B'}C4$ and P_BC1 coupling. The reason behind this being that each phosphorus atom is approximately transoid to its respective carbon. The smaller coupling , ($^2J_{PC} = 5.00$ Hz) , is then attributable to $P_{B'}C1$ and P_BC4 coupling , this assignment being strengthened by the approximate cisoid configuration of each phosphorus atom to its respective carbon.

Although the phosphorus atoms , (P_B) , are considered to be chemically equivalent , spin-spin coupling still occurs between them. This coupling cannot be observed by direct ^{31}P n.m.r spectroscopy , however one unexpected bonus of the computer simulation of the ^{13}C n.m.r spectrum is that all the P,P- couplings are obtained. That is the P_AP_B coupling already observed in the phosphorus n.m.r spectrum and the $P_BP_{B'}$ coupling , ($^2J_{PP} = 28.6$ Hz) not previously seen. The larger value of $J(P_BP_{B'})$, (when compared to that of P_AP_B) , would seem to suggest that the P_B-

Ru - P_B angle is much closer to 90° than the P_A- Ru - P_B angle. The crystal structure of [$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$] , would seem to support this , the P_B - Ru - P_B angle , (94.6°) , being closer to 90° than the P_A- Ru - P_B angle , (96.7°). Although the difference in angles is not that marked it would seem to have a significant effect on the P,P- spin-spin coupling.

Finally , while it has been said that C,H- and C,C- coupling constants also give a great deal of structural information , the complex nature of the spectra obtained for these complexes prevents identification of such couplings in this case.

2.6 Use of the di-Grignard [o-$C_6H_4(CH_2MgCl)_2$]

Reaction of the di-Grignard reagent , [o-$C_6H_4(CH_2MgCl)_2$] with [$RuCl_2(PPh_2Me)_4$] in tetrahydrofuran leads to the o-xylidene compound [$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$] , (figure 2.30) , a result

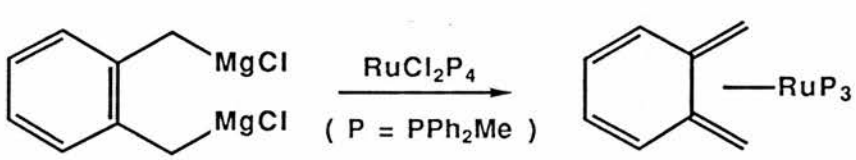


Figure 2.30

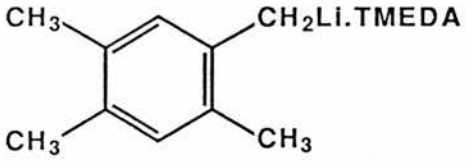
that is not unexpected considering Lappert's observations and Dixneuf's work with iron. This then provides yet another route to

o-xylidenes of ruthenium.

2.7 Preparation of [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)P_3$]

Following the successful development of a synthetic route to [$Ru(CH_2C_6H_4CH_2)P_3$] , ($P = PMe_3$, PMe_2Ph , PPh_2Me) , from the parent alkane , an extension of the procedure to prepare ring substituted o-xylidenes was sought. Initially , the preparation of a complex containing a substituted o-xylidene , which was not very different from the parent o-xylidene , was attempted. With the prerequisite of the reaction for an organic precursor with two methyl groups ortho to one another , preparation of an o-xylidene ruthenium complex based on 1,2,4,5-tetramethylbenzene , (durene) , was attempted. Durene is completely symmetrical and therefore ensures that if mono-metallation is achieved only one product should be formed. Further because of the symmetrical nature of the ligand and its similarity with o-xylene the characterization should be straightforward.

Very little work has been undertaken on the metallation of durene but from the work that has been published[95] it is reasonably safe to assume once again that a 1 : 1 ratio of BuLi-TMEDA should produce predominantly the monolithiated species , (**69**) , (figure 2.31).

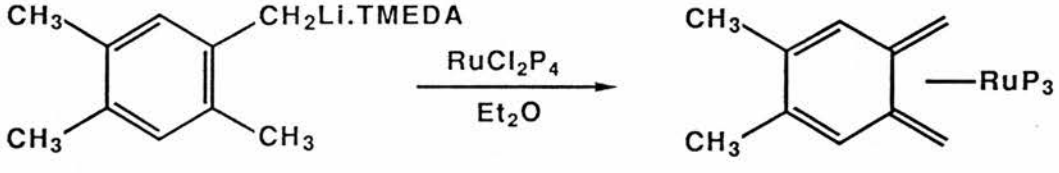


(69)

Figure 2.31

2.7.1 Procedure

Reaction of [$RuCl_2P_4$] , ($P = PMe_3$ or PPh_2Me) , with two or more mole equivalents of 1-lithiomethyl-2,4,5-trimethylbenzene.TMEDA at room temperature in diethyl ether leads to compounds analyzing as [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)P_3$] , (**70**) , (figure 2.32).



(70)

(P= PMe_3 or PPh_2Me)

Figure 2.32

The ^1H n.m.r spectrum shows the expected multiplets due to the ,

endo , (H_A) , and exo , (H_B) hydrogens of the methylene groups confirming the η^4-binding. With the replacement of two of the ring hydrogens of the o-xylidene ligand by methyl groups , the low field region becomes much simpler , a single resonance for the remaining two ring hydrogens is observed , confirming , as expected the plane of symmetry running through the ligand.

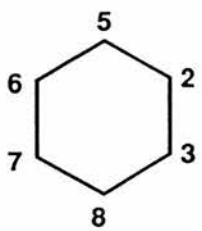
In the ^{31}P n.m.r spectra there are two resonances in the ratio 1 : 2 and assignable to the unique , (P_A) , and symmetry related , (P_B) , phosphorus atoms. Once again there is the unusually small coupling between the two sets of atoms reflecting the P - Ru - P angles near 100°.

In fact the n.m.r spectra of [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)P_3$] present very little additional structural information but do allow us to confirm their characterizations as substituted o-xylidene ruthenium complexes.

Comparison of the spectra of [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PMe_3)_3$] with those of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] does enable further completion of spectral assignments , (figure 2.33).

The ^{13}C n.m.r spectrum of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] has two resonances , (δ 122.97 and δ 131.65) , which are due to the C5,C8 and C6,C7 carbons of the o-xylidene ligand. It is difficult however to assign either resonance to a particular pair of carbons. In considering the ^{13}C n.m.r spectrum of

[$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PMe_3)$] , the C6 and C7 carbons are



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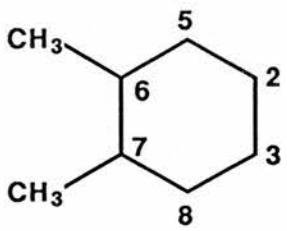


(72)

	δ (ppm)	
Carbons	(71)	(72)
C2 , C3	101.65	100.32
C5 , C8	131.65	131.06
C6 , C7	122.97	130.64

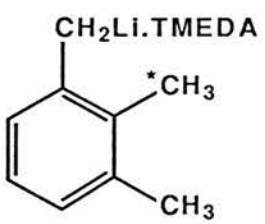
Figure 2.33

now quaternary carbons and so are easily identifiable , (δ 130.64) , by the low intensity of the signal. The remaining unidentified signal must be the resonance of the C5,C8 carbons. The effect of the methyl groups adjacent to carbons C6 and C7 is similar to that observed when comparing the ^{13}C n.m.r of benzene and o-xylene. A mesomeric effect created by the methyl groups deshields the C6 and C7 carbons and shifts the signal to lower field. The corresponding signal for the C6 and C7 carbons of [$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$] should therefore be at higher field

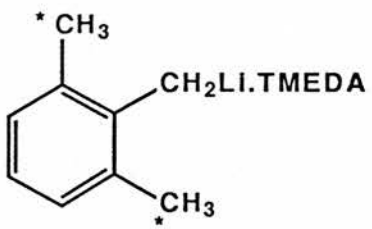
and is the signal at δ 122.97. The signal at δ 131.65 is therefore now identifiable as that for the C5,C8 carbons.

2.8 Preparation of [$Ru(CH_2C_6H_3\{CH_3\}CH_2)P_3$]

Work by Klein and Medlik-Balan [95] shows that metallation of 1,2,3-trimethylbenzene with a 1 : 1 ratio of BuLi-TMEDA produces a mixture of 1-lithiomethyl-2,3-dimethylbenzene,



(73)



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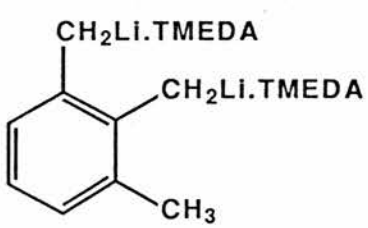


(75)

*** indicates possible position of δ-hydrogen abstraction**

Figure 2.34

(**73** ,30%) , 1-lithiomethyl-2,6-dimethylbenzene , (**74** ,16%) , and

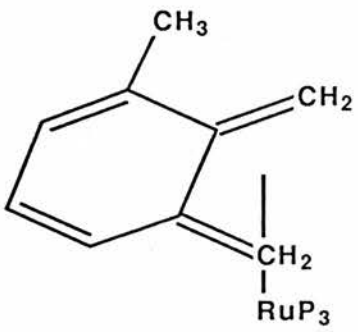
bis(1,2-lithiomethyl)-3-methylbenzene , (**75** ,31%) ,
(figure 2.34). Although three different products are obtained when metallating 1,2,3-trimethylbenzene , a consideration of the requirements of the reaction to produce an o-xylidene complex of ruthenium suggests that all three should produce the same unsymmetrical methyl-substituted o-xylidene.
The important step of the reaction when considering the mono-metallated species is the δ-hydrogen step. In these compounds δ-hydrogen abstraction can only take place on a methyl group in an ortho position to the metallated methyl. For (**73**) therefore δ-hydrogen abstraction can only take place at one position , for (**74**) there are two possible sites for δ-hydrogen abstraction , each possibility results in the same product. The dilithiated species should act in a similar manner to Lappert's and Dixneuf's compounds and again produce the same product.

It is expected that with (**74**) two enantiomers , (**76**) and (**77**) , (figure 2.35) , will be obtained.

If the metal lies below the plane of the o-xylidene ligand then one enantiomer would have the methyl substituent on the ring , to the right of the metal and the other to the left.

A procedure similar to that mentioned previously results in compounds analyzing as [$Ru(CH_2C_6H_3\{CH_3\}CH_2)P_3$] , ($P = PMe_3$

or PPh_2Me).



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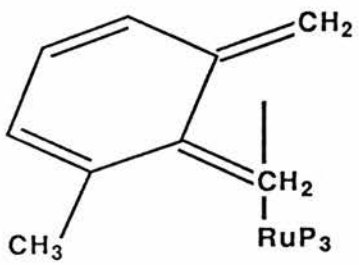


(77)

Figure 2.35

As expected of unsymmetrical compounds the n.m.r data is much more complex than for the symmetrical o-xylidenes.

2.8.1 ^1H n.m.r

In the ^1H n.m.r , (figure 2.36) , three signals are observed for the phosphine groups , indicating that all three groups are inequivalent. The methyl groups on each resonate as doublets , and can be assigned by their P,H- coupling constants. The larger P,H-coupling , (c.a 7 Hz) , is attributable by comparison with the ^1H n.m.r spectra of [$Ru(CH_2C_6H_4CH_2)P_3$] , to the unique , (P_A) , phosphine group. The remaining two resonances , with P,H-

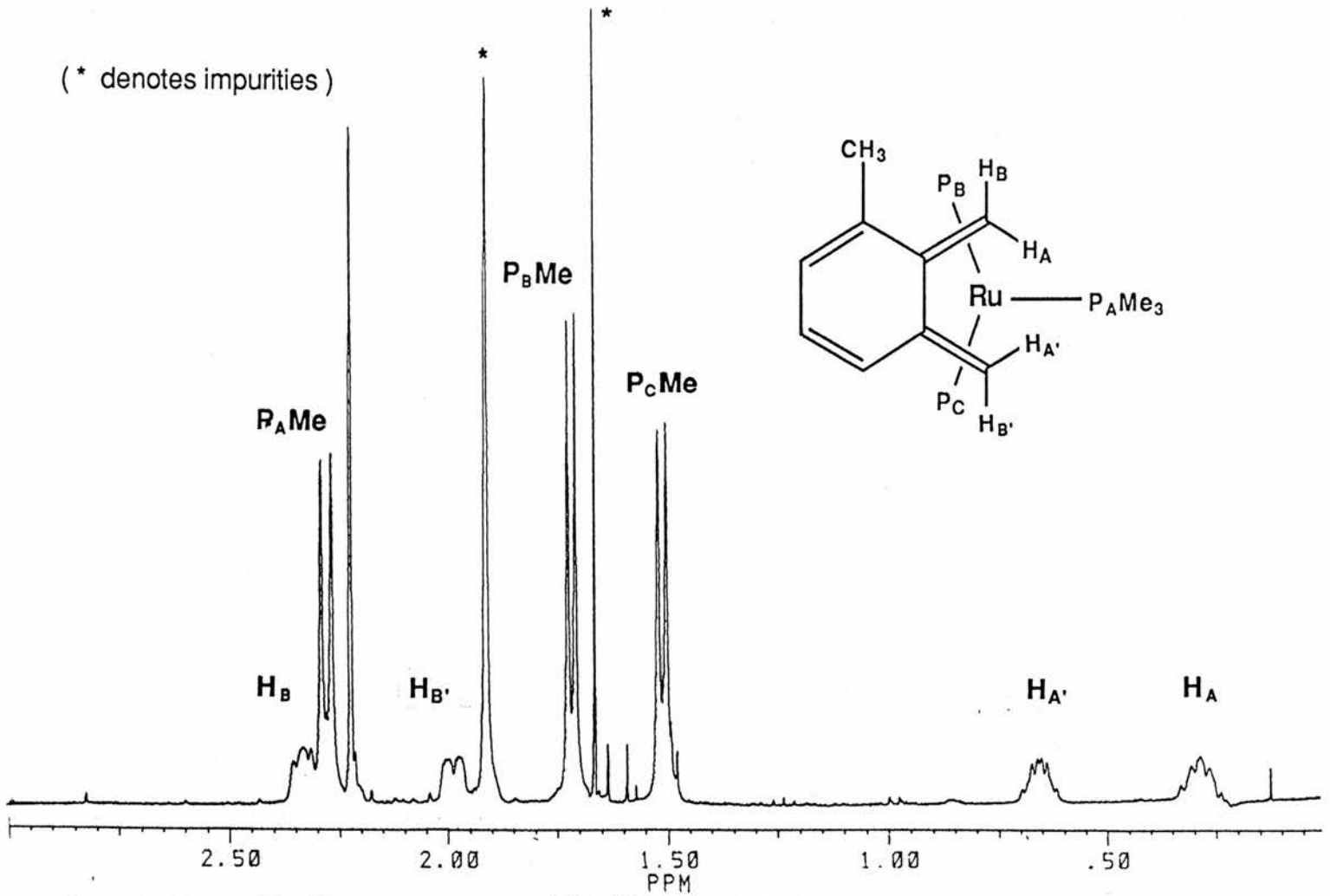
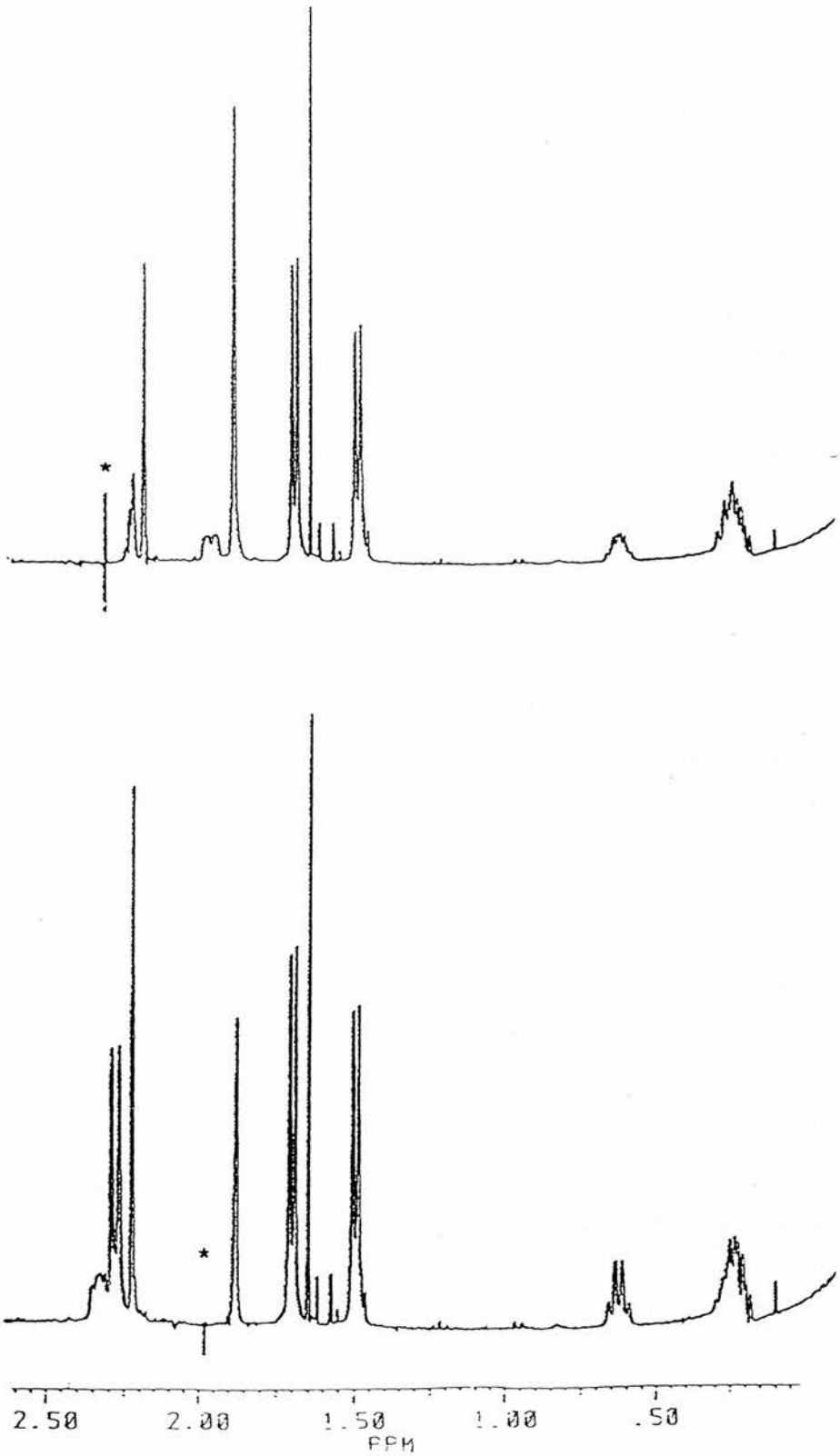
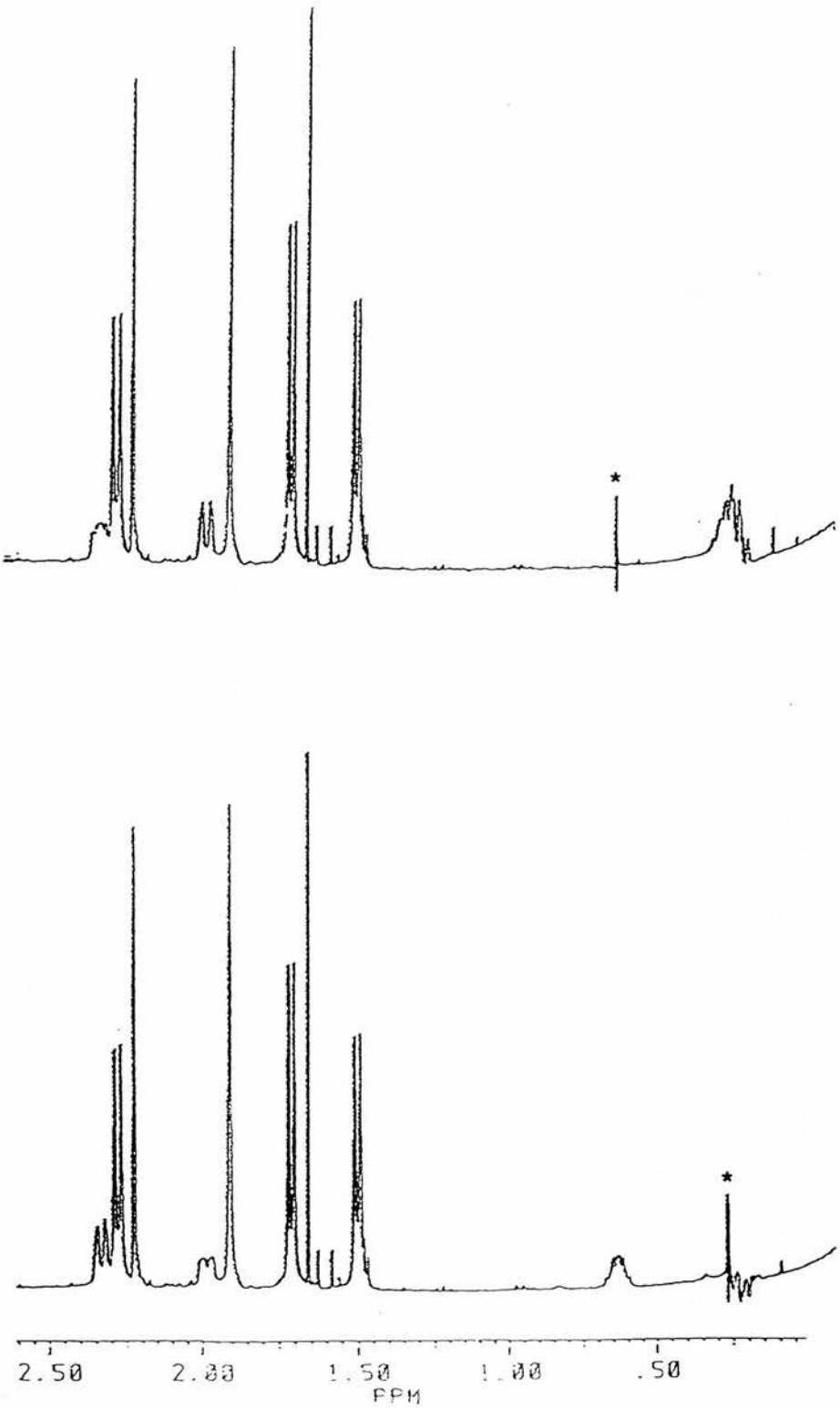


Figure 2.36 The ^1H n.m.r spectrum of $[Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3]$ (300 MHz) (C_6D_6, 25°C)



The ^{1}H n.m.r spectrum of $[Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3]$
(300 MHz) (C_6D_6, 25°C)
(* denotes the position of the decoupler)

Figure 2.37



The ^{1}H n.m.r spectrum of $[Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3]$
(300 MHz) (C_6D_6, 25°C)
(* denotes the position of the decoupler)

Figure 2.38

couplings , (c.a 5 Hz) , again by comparison are obviously the more similar , (P_B and P_C) , phosphine groups.

As with the symmetrical o-xylidene complexes the resonances due to the methylene hydrogens are particularly distinctive. Four multiplets are observed for these hydrogens , two of which are shifted to high field. Each multiplet would seem to represent the resonance of one methylene hydrogen. The complex pattern of each multiplet suggests coupling to the adjacent hydrogen and further couplings to all three phosphorus atoms.

A series of homonuclear decoupling experiments , (figures 2.37 and 2.38) , similar to those performed earlier , indicates that there is coupling between the hydrogens on each methylene carbon group , (H_AH_B , $H_{A'}H_{B'}$) , and that there is no coupling between the groups.

2.8.2 ^{31}P n.m.r

The ^{31}P n.m.r spectra , (figure 2.39) , show three resonances assignable to the three inequivalent phosphorus atoms. The most distinct , (P_A) , phosphorus atom resonates as a singlet , (P = PPh_2Me , $^2J(P_AP_B) < 2$ Hz , $^2J(P_AP_C) < 2$ Hz) , and a pseudotriplet , (P = PMe_3 , $^2J(P_AP_B) = 8.48$ Hz , $^2J(P_AP_C) = 8.37$ Hz). The more closely related , (P_B and P_C) , phosphorus atoms resonate as doublets ,(P = PPh_2Me , $^2J(P_BP_C) = 22.51$ Hz) ,

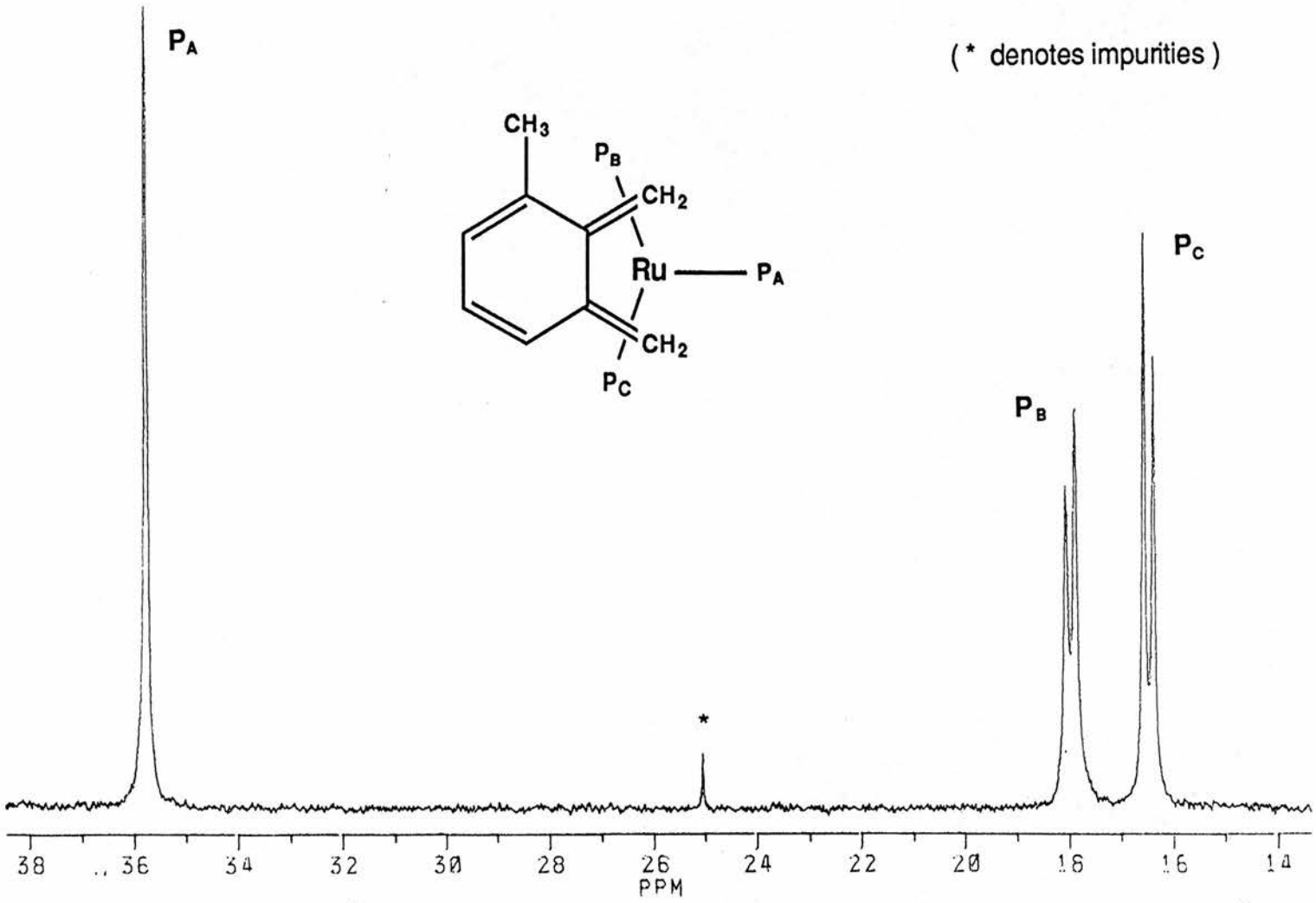


Figure 2.39 The ^{31}P-{^{1}H} n.m.r spectrum of [$Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3$] ($C_6D_6$, 25°C)

Figure 2.40 Selected ^1H n.m.r data for the new quinodimethane complexes [a]

Compound	P_AMe (J_{PH})	P_BMe (J_{PH})	P_CMe (J_{PH})	CH_{exo} (J_{PH})	CH_{endo} (J_{PH})	(J_{HH})
[$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$]	2.22 d(7.0)	1.69 pd(4.3)[b]		1.99 dd(5.9)	0.68 dd(6.9)	3.9
[$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$]	1.42 d(7.9)	1.03 pd(5.9)[b]		1.96 dd(5.6)	- 0.04 dd(6.6)	3.7
[$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PPh_2Me)_3$]	2.24 d(7.0)	1.73 pd(4.4)[b]		1.96 dd(6.1)	0.73 dd(7.1)	3.4
[$Ru(CH_2C_6H_2\{CH_3\}_2CH_2(PMe_3)_3$]	1.45 d(7.3)	1.03 pd(5.3)[b]		1.95 dd(5.6)	0.00 dd(7.0)	3.5
[$Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3$]	2.28 d(7.1)	1.71 d(5.2)	1.51 d(5.2)	2.33 m , 1.98 m	0.64 m , 0.27 m	
[$Ru(CH_2C_6H_3\{CH_3\}CH_2)(PMe_3)_3$]	1.44 d(7.8)	1.07 d(6.1)	1.04 d(6.1)	2.17 m , 1.91 m	- 0.16 m , - 0.22 m	

[a] Chemical shifts in ppm to high frequency of $SiMe_4$, coupling constants in Hz ; measured in C_6D_6 at 298K using C_6D_5H (δ 7.27) as internal reference ; s = singlet , d = doublet , t = triplet , m = multiplet , p = pseudo.

[b] $J_{PH} + J_{PH'}$

Figure 2.41 ^{31}P n.m.r data for the new quinodimethane complexes

Compound	Chemical Shifts [a]			Coupling Constants (J , Hz)		
	P_A	P_B	P_C	P_AP_B	P_AP_C	P_BP_C
[$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$]	36.03 (s)	20.42 (s)		< 2	< 2	-
[$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$]	14.87 (t)	- 8.38 (d)		8.72	8.72	-
[$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PPh_2Me)_3$]	35.18 (s)	21.45 (s)		< 2	< 2	-
[$Ru(CH_2C_6H_2\{CH_3\}_2CH_2(PMe_3)_3$]	13.97 (t)	- 5.46 (d)		7.27	7.27	-
[$Ru(CH_2C_6H_3\{CH_3\}CH_2)(PPh_2Me)_3$]	35.82 (s)	17.87 (d)	16.40 (d)	< 2	< 2	22.51
[$Ru(CH_2C_6H_3\{CH_3\}CH_2)(PMe_3)_3$]	14.25 (t)	- 7.60 (dd)	- 11.25 (dd)	8.48	8.37	29.46

[a] Chemical shifts in ppm to high frequency of external 85% H_3PO_4 , measured in C_6D_6 at 298K.

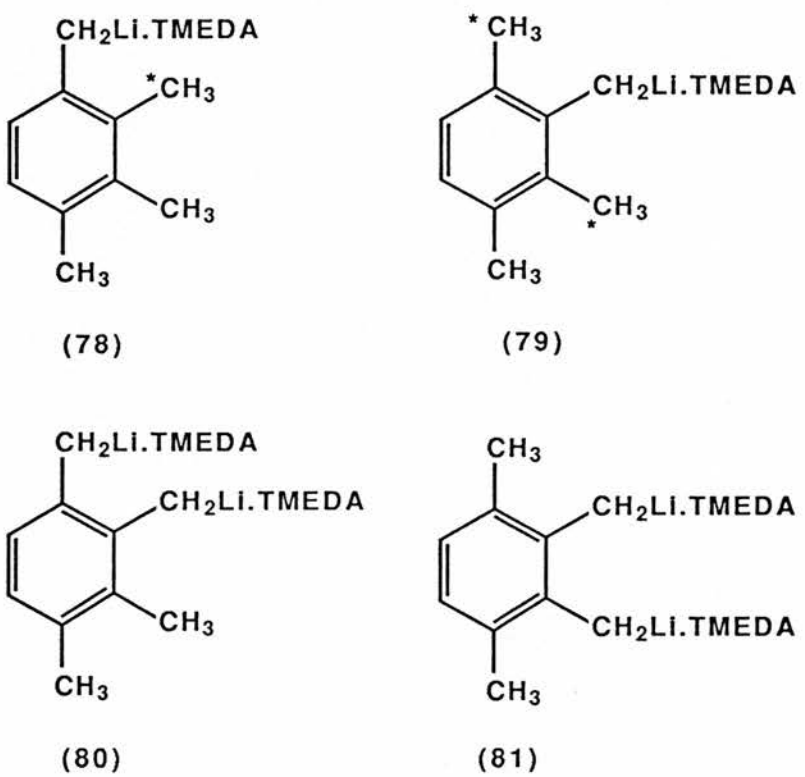
and as doublets of doublets , (P = PMe_3 , ^2J (P_BP_C) = 29.46 Hz). In each case the phosphorus coupling constants compare very favourably with those of the symmetrical o-xylidene complexes of ruthenium , and suggest therefore that there is no significant change in the RuP_3 fragment of the complex.

A summary of the ^1H n.m.r and ^{31}P n.m.r data for the o-xylidene complexes of ruthenium is presented in the following tables , (figure 2.40 and figure 2.41).

2.9 Preparation of [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PMe_3)_3$]

Use of 1,2,3,4-tetramethylbenzene as a precursor should allow for the synthesis of both symmetrical and unsymmetrical methyl-substituted o-xylidenes of ruthenium.
Results of metallation on the previous polymethylbenzene compounds would suggest that metallation with BuLi-TMEDA should produce a mixture of mono - and dilithiated species. Included should be the compounds , 1-lithio-2,3,4-trimethylbenzene .TMEDA , (**78**) , 1-lithiomethyl-2,3,6-trimethylbenzene.TMEDA , (**79**) , bis(1,2-lithiomethyl)-3,4-dimethylbenzene.TMEDA , (**80**) , and bis(1,2-lithiomethyl)-3,6-dimethylbenzene.TMEDA , (**81**) , (figure 2.42) , which should be capable of producing o-xylidene complexes of ruthenium. It is interesting that while (**78**) and (**80**) should react to form an unsymmetrical o-xylidene and

(**81**) to a symmetrical o-xylidene , there are two possible positions of δ-hydrogen abstraction for (**79**) , one of which produces an unsymmetrical o-xylidene and the other a symmetrical o-xylidene.



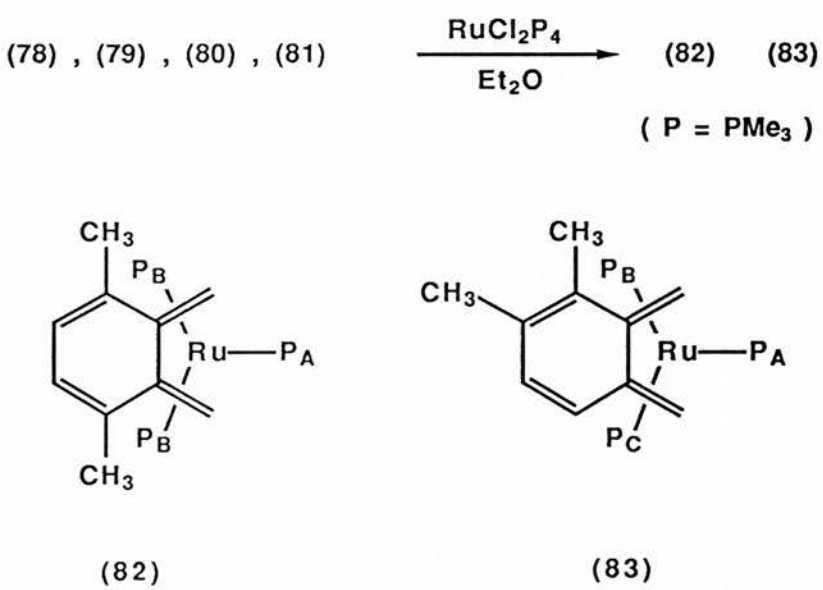
*** indicates possible position of δ-hydrogen abstraction**

Figure 2.42

It is unfortunate that data is not available concerning the relative proportions of each metallated product to investigate the possibility of preferential δ-hydrogen abstraction on steric or electronic grounds.

The synthesis again employs a procedure similar to that mentioned previously and results in a compound analyzing as [$Ru(CH_2C_6H_2\{CH_3\}_2CH_2)(PMe_3)_3$] , (figure 2.43).

Statistics on the mono-metallation of 1,2,3,4-tetramethylbenzene suggest that if if metallation is equally likely on any methyl then a 2 : 1 ratio of unsymmetrical to symmetrical products should be obtained. Perhaps coincidentally , the ^{31}P n.m.r of the reaction solution shows the presence of both the unsymmetrical and symmetrical o-xylidene complexes in an approximate ratio of 2 : 1.



(82) (83)

Figure 2.43

The ^{31}P n.m.r of the symmetrical product , (**82**) , shows two resonances of approximate ratio 1 : 2 , a triplet , (δ 14.25 , $^2J_{PP}$ =

7.92 Hz) , and a doublet , (δ - 10.85 , $^2J_{PP}$ = 7.92 Hz) , assigned to the unique , (P_A) , and symmetry related , (P_B) , phosphorus atoms respectively.

The unsymmetrical o-xylidene , (**83**) , has a spectrum typical of an ABX spin system with appropriate assignments ; P_A : (δ 14.78 , $^2J_{PP}$ = 7.36 Hz , $^2J_{PP}$ = 8.01 Hz) ; P_B : (δ - 7.62 , $^2J_{PP}$ = 7.36 Hz , $^2J_{PP}$ = 29.13 Hz) ; P_C : (δ - 7.89 , $^2J_{PP}$ = 8.01 Hz , $^2J_{PP}$ = 29.13 Hz).

For both complexes the chemical shifts and coupling constants obtained from the ^{31}P n.m.r spectrum are in complete agreement with those observed for other symmetrical and unsymmetrical o-xylidene complexes of ruthenium discussed in this chapter.

Whilst both products are observed in the reaction solution , crystallization yields only the unsymmetrical product. The symmetrical complex remains in solution. This can perhaps be explained as a consequence of the larger quantity of unsymmetrical complex present.

The ^1H n.m.r of the crystallized product is very much as expected for the unsymmetrical product. The AB pattern at low field confirms the lack of a plane of symmetry running through the centre of the o-xylidene ligand. The methyl groups on the unique phosphorus atom , (P_A) , resonate as a doublet , ($^2J_{PH}$ = 7.8 Hz) , those of the more similar phosphorus atoms , (P_B and P_C) , also as doublets , ($^2J_{PH}$ = 5.8 Hz and 6.0 Hz). Lastly there are the

expected multiplets due to the endo , (H_A) , and exo , (H_B) , hydrogens of inequivalent methylene groups , confirming the η^4-binding.

2.10 Auxiliary Ligands

As has been mentioned in chapter one (see section 1.6) , it appears that the type of ligands in a particular o-xylidene complex have a bearing on the type of bonding present. Poor acceptor ligands such as cyclopentadiene tend to favour σ^2- or σ^2,π- bonding , while good acceptor ligands such as carbonyls favour π^2- bonding.

The advantage of using tertiary phosphines as ligands in organometallic synthesis lies in the recognition that changing substituents on phosphorus ligands can cause marked changes in the behaviour of their transition metal complexes.

Identification of the bonding in the new o-xylidene complexes of ruthenium , with ligands of the type PMe_3 , PMe_2Ph , and PPh_2Me , as being intermediate σ^2,π- and π^2- would seem to suggest that all three of these tertiary phosphines are acting as fairly good π-acceptor ligands , even though they are more usually described as σ-donors .

As probably the most commonly used phosphorus (III) ligand ,

and a better π-acceptor than PMe_3, PMe_2Ph or PPh_2Me, it might be questioned why triphenylphosphine is not used as a counter ligand. There is the added advantage that [$RuCl_2(PPh_3)_{3\ or\ 4}$] is a well known and easily prepared complex [96]. Numerous attempts at preparing o-xylidene complexes of ruthenium containing triphenylphosphine ligands have been made but in no case has such a complex been observed. Whilst prior to 1970 nearly everything was rationalized in terms of electronic effects, it has since become increasingly apparent that steric effects are generally at least as important and can dominate in many cases. A comparison of the electronic and steric parameters of the tertiary phosphine ligands which have produced o-xylidene complexes with those of triphenylphosphine suggest that while the electronic effects of the ligands are not so different, the large cone angle, ($\theta = 145^o$) of the triphenylphosphine ligand is probably the dominant factor in preventing the formation of an o-xylidene complex [97].

Triphenylphosphite has a cone angle, ($\theta = 128^o$), very much less than that of triphenylphosphine and can be considered as a much better π-acceptor, and should therefore have a greater tendency for π^2-bonding in o-xylidene complexes than the phosphine ligands used previously.

2.11 Preparation of $[RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3]$

Reaction of $[RuCl_2(P(OPh)_3)_4]$ with two or more equivalents of 1-lithiomethyl-2-methylbenzene.TMEDA at room temperature, in diethyl ether leads to a white crystalline solid.

^1H n.m.r

The complexity of the low-field aromatic region of the spectrum is in accordance with the presence of a number of triphenylphosphite groups, and yields very little additional information. More importantly at higher field only a single resonance, δ 2.3 (toluene of crystallization), is observed and confirms the lack of an o-xylidene ligand, (figure 2.44). A band at 1910 cm^{-1} in the infra-red spectrum of the compound can be attributed to ν(Ru-H). An examination of the region of the ^1H n.m.r spectrum in which hydride resonances are normally found, (figure 2.45), shows agreement with the infra-red information and indicates the presence of a hydride group at δ - 7.8 with coupling to four phosphorus atoms, (doublet of quartets, $^2J_{PH}$ trans = 129.79 Hz; $^2J_{PH}$ cis = 21.65 Hz; $^2J_{PH}$ cis = 25.79 Hz; $^2J_{PH}$ cis = 21.95 Hz).

A complex of the form $[RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3]$ is

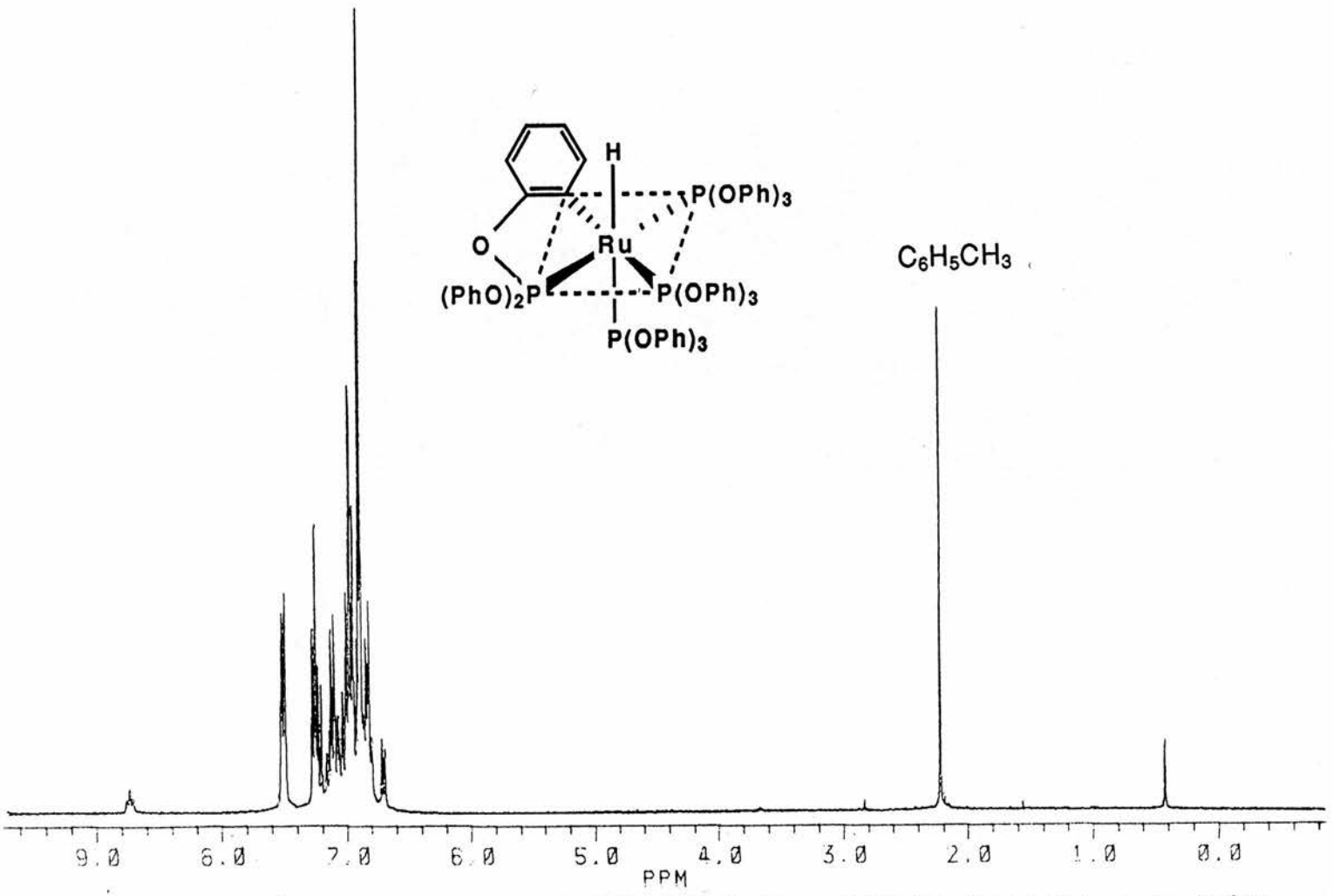
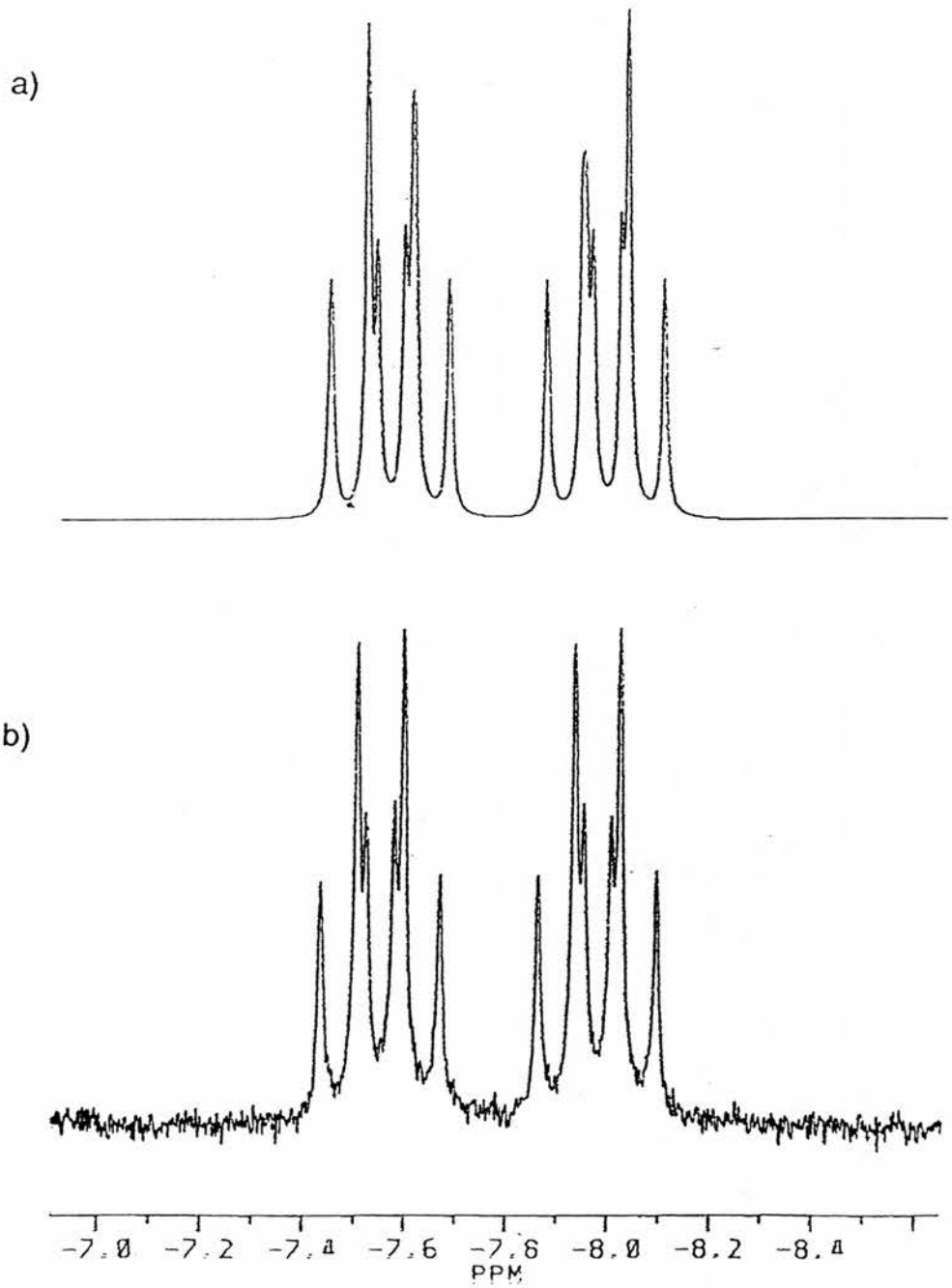


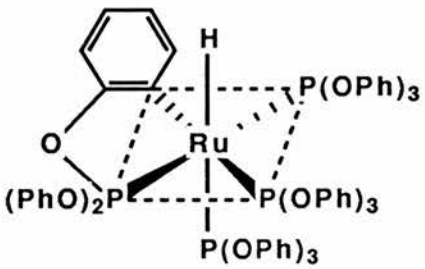
Figure 2.44 The ^{1}H n.m.r spectrum of $[RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3]$ (300 MHz) (C_6D_6, 25°C)



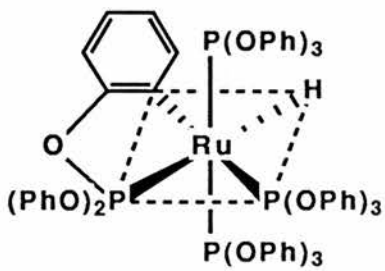
The hydride region of the
^{1}H n.m.r spectrum of $[RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3]$

a) PANIC simulated spectrum
b) Experimental spectrum

Figure 2.45



(84)



(85)

Figure 2.46

suggested , (figure 2.46) , with possible structures (**84**) or (**85**) , in which there is a σ-bond between an ortho-carbon atom of the triphenylphosphite ligand and the metal centre. Many examples of this type of interaction , between the central metal atom and an ortho-carbon atom of a phenyl group on a triphenylphosphine ligand are known [98]. The five-membered chelate ring structures suggested for the ruthenium - carbon bonded triarylphosphite complexes are expected to be less sterically strained than the four-membered rings found in the related metal-carbon bonded triphenylphosphine derivatives. Thus on steric grounds at least , metal-ortho-carbon bond formation will occur more readily in the complex chemistry of triarylphosphites than in that of triarylphosphines.

^{31}P n.m.r

Analysis of the ^{31}P n.m.r spectrum (by PANIC simulation) ,

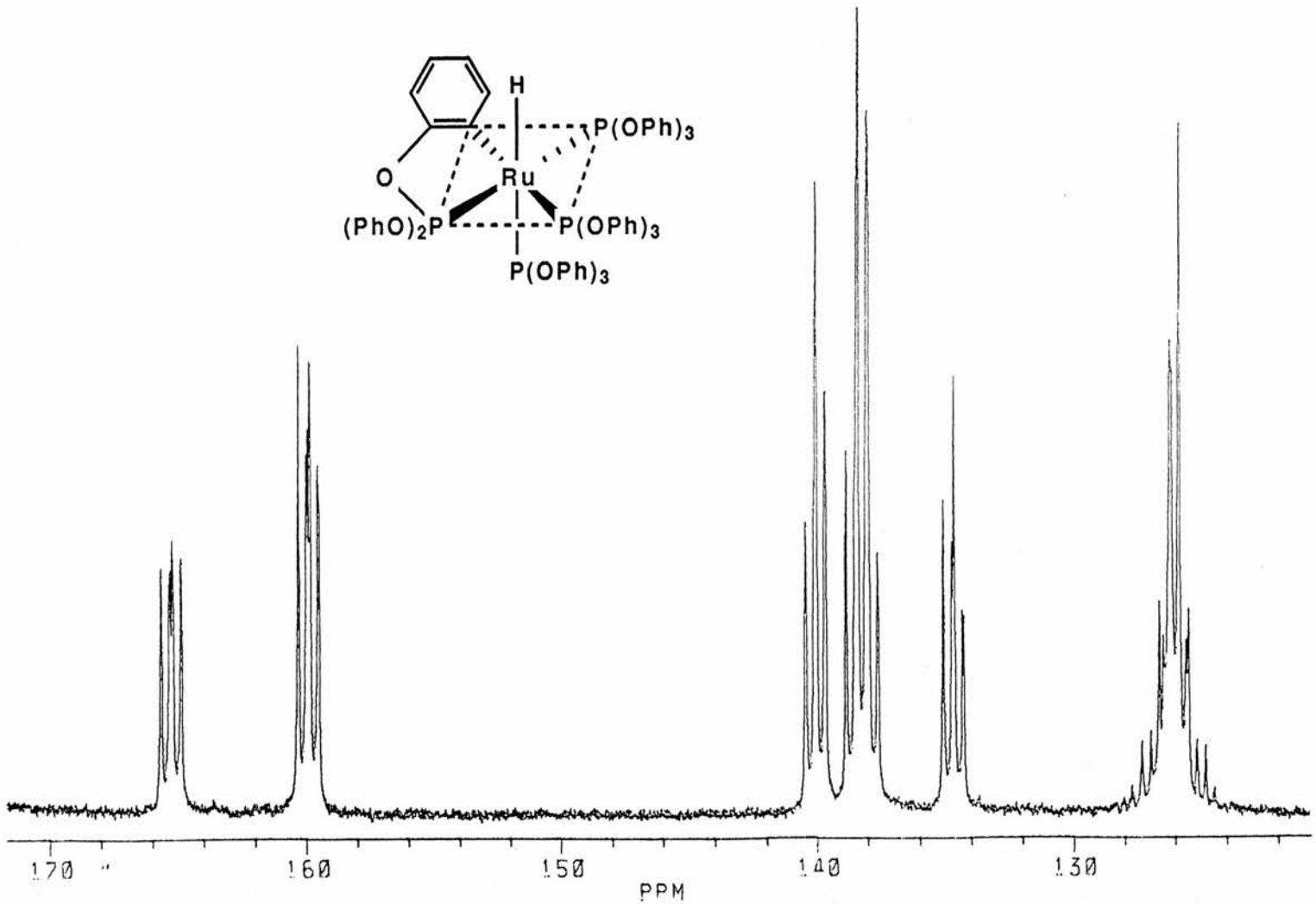


Figure 2.47 The ^{31}P-{^{1}H} n.m.r spectrum of $[RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3]$ (C_6D_6, 25°C)

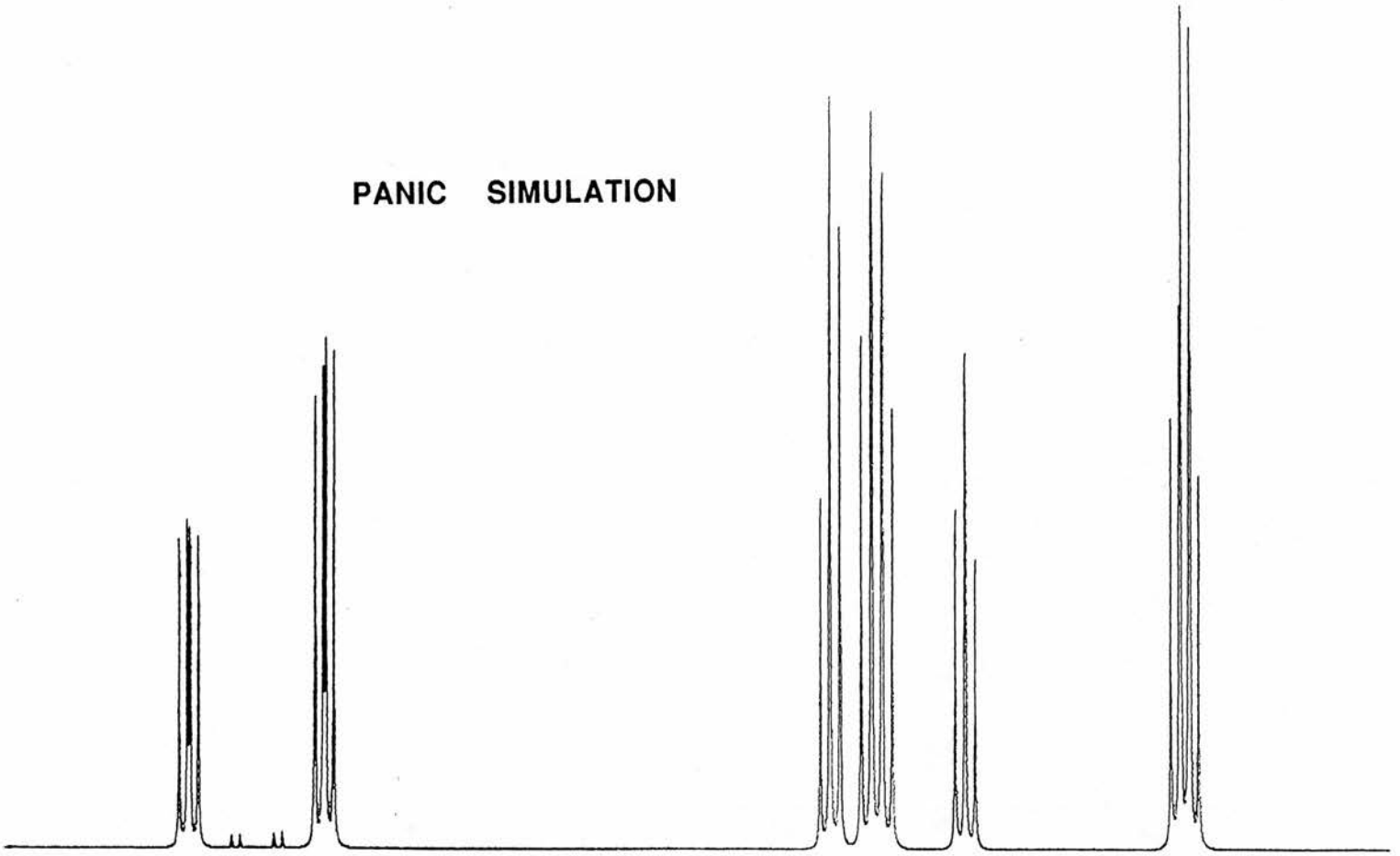
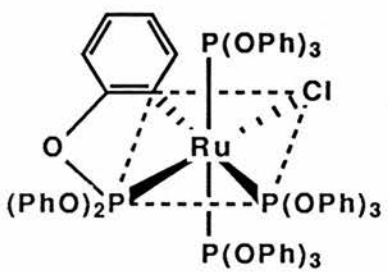


Figure 2.48 The ^{31}P-{^{1}H} n.m.r spectrum of [RuH($C_6H_4OP(OPh)_2$)($P(OPh)_3$)$_3$] (C_6D_6, 25°C)

(figures 2.47 and 2.48), confirms the presence of four ineqivalent phosphorus ligands, δ 163.28 ; δ 138.96; δ 138.38 ; and δ 126.69 , relative intensities 1 :1 : 1 : 1.



(86)

Figure 2.49

A comparison can be made with the analogous compound [$RuCl(C_6H_4OP(OPh)_2)(P(OPh)_3)_3$] [99,100], (**86**), (figure 2.49). The ^{31}P n.m.r for this compound consists of two pairs of triplets and one pair of doublets with relative intensities 1 : 1 : 2 , and clearly suggests a structure similar to (**84**) and (**85**). The two axial phosphorus ligands are equivalent and no <u>trans</u> coupling is seen. In fact all the observable P-P couplings are in the same range (40 - 60 Hz), which suggests that all the interactions are similar, (i.e <u>cis</u>).

This comparison would clearly seem to discount (**85**) as a possible structure for [$RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3$] since all the phosphorus atoms are shown to be inequivalent. Confirmation

of the structure as being (**84**) is provided by a <u>trans</u> P-P coupling , ($^{2}J_{PP}$ <u>trans</u> = 641.95 Hz) between the phosphorus atoms resonating at δ 163.28 and δ 138.38. Such a substantial difference in chemical shift would not be expected if the two phosphorus ligands were the same [101].

2.12 Mechanistics

It has already been established that the reaction has a requirement for two moles of alkylating agent , (further details of the mechanism are discussed in chapter 3). The scheme (figure 2.50) offers an account for the formation of the o-xylidene complexes of ruthenium . Two transmetallation reactions of 1-lithiomethyl-2-methylbenzene.TMEDA , together with loss of phosphine can be expected to lead to the 16-electron intermediate (**87**). This coodinatively unsaturated ruthenium center bonded to basic phosphines should favour either a δ (C-H-Ru) two-electron agostic interaction or a δ (C-H) oxidative addition. Elimination of o-xylene would then lead to complexes of the type (**88**). Formation of [$RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3$] and unsuccessful attempts by Dixneuf to prepare [$Fe(CH_2C_6H_4CH_2)(P(OMe)_3)_3$] in which carbon-carbon coupling to form (**89**) was observed , (figure 2.51) , would seem to further support the theory of the two transmetallation reactions.

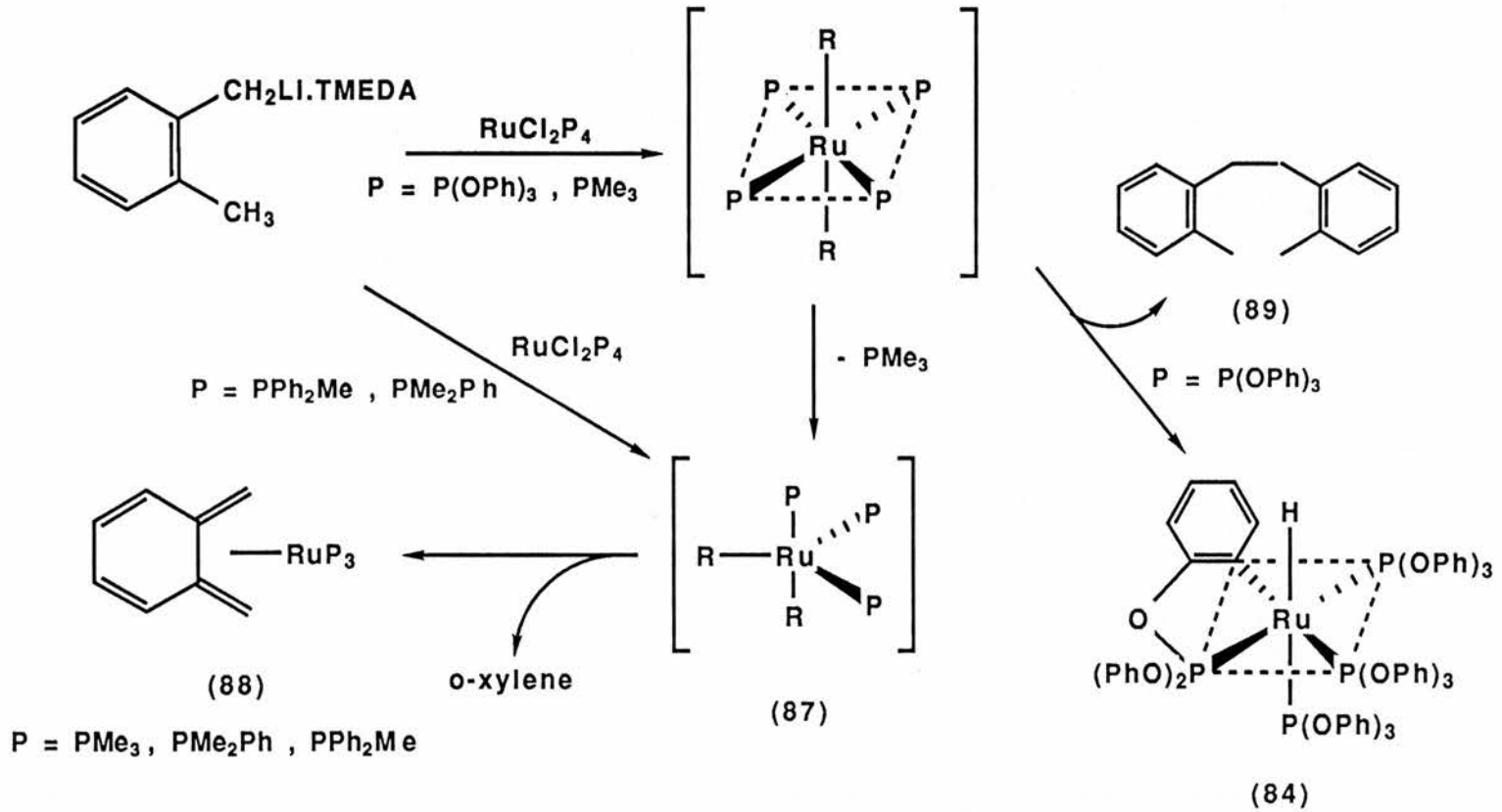
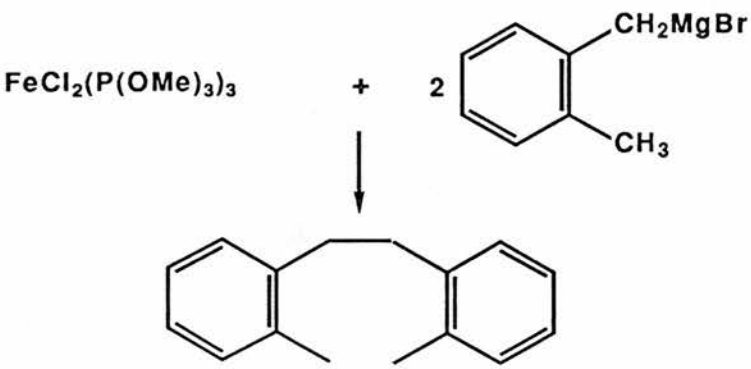

CH2LI.TMEDA
CH3
RuCl2P4
P = P(OPh)3 , PMe3
R
P
Ru
(89)
RuCl2P4
P = PPh2Me , PMe2Ph
- PMe3
P = P(OPh)3
RuP3
(88)
o-xylene
(87)
H
O
(PhO)2P
P(OPh)3
(84)
P = PMe3 , PMe2Ph , PPh2Me

Figure 2.50



(89)

Figure 2.51

In the case where $P = P(OPh)_3$, loss of phosphite is not the favoured process , instead there is effective reductive elimination of the alkyl groups together with rearrangement of the 16-electron complex to form the more stable 18-electron complex , (**84**).

In questioning the role the phosphine and phosphite ligands have in determining the reaction pathway , important points to note are the reluctance of [$RuCl_2(P(OPh)_3)_4$] to lose a phosphite ligand and that the presence of phosphite ligands would give a 16-electron ruthenium (II) intermediate with a less electron rich centre than when using PMe_3, PMe_2Ph , or PPh_2Me. Thus the δ (C-H) oxidative addition required to form an o-xylidene complex would be expected to be disfavoured compared with reductive elimination and carbon - carbon bond formation. The formation of

the zero-valent ruthenium complex promotes C-H addition to reduce the electron density on the ruthenium and give the observed product.

2.13 Electrochemical Study

The cyclic voltammetry of [$Ru(CH_2C_6H_4CH_2)P_3$] , (P = PPh_2Me and PMe_3) was studied in dichloromethane (figure 2.52). The

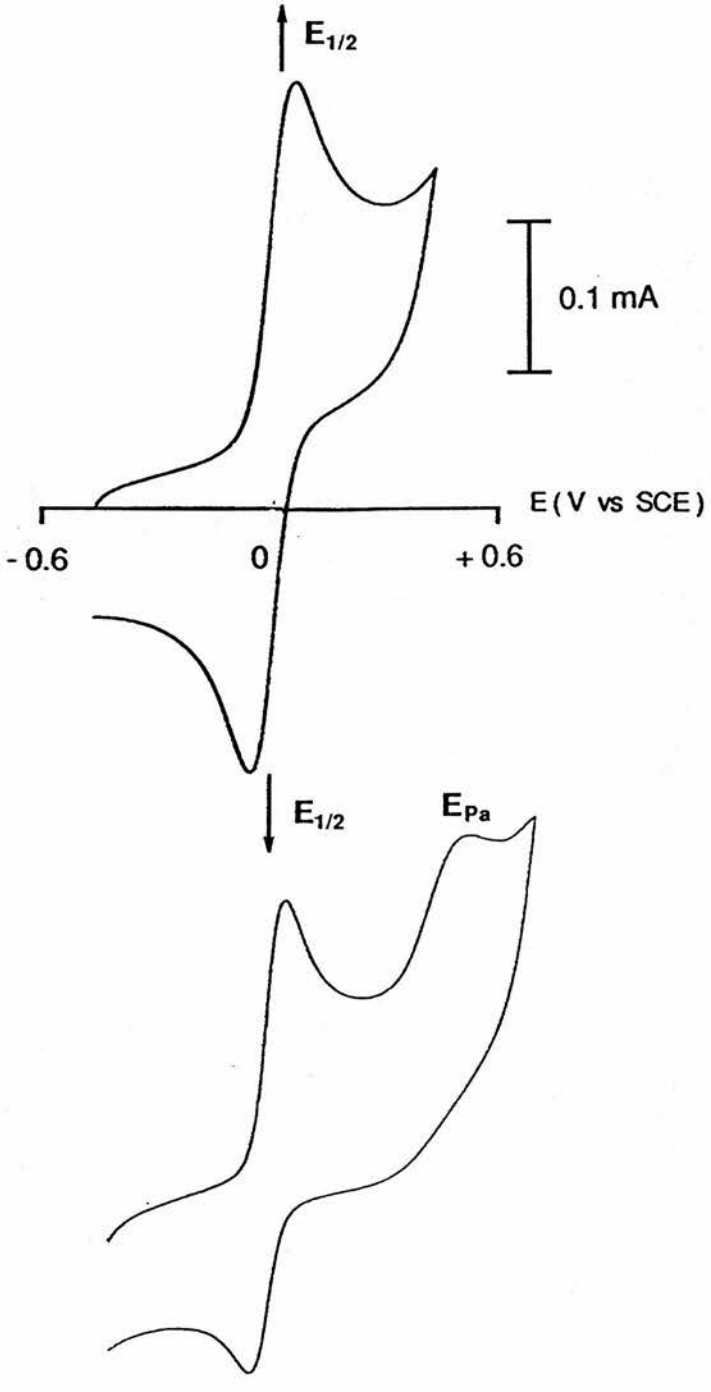
Cyclic Voltammetry Data [a]

Complex	1st Wave $E_{1/2}$, V	2nd Wave [b] E_{Pa} , V
[$Ru(CH_2C_6H_4CH_2)(PMe_3)_3$]	- 0.19	0.46
[$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$]	0.05	0.71

[a] At a platinum electrode in CH_2Cl_2 solutions containing 0.1 M Bu_4NPF_6. Scan rate 200 mVs^{-1}. Potentials are reported relative to potassium chloride SCE. [b] Irreversible wave.

Figure 2.52

cyclic voltammogram of [$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$] is shown (figure 2.53). A reversible one-electron oxidation corresponds to the formation of [$Ru(CH_2C_6H_4CH_2)P_3$]$^+$ which can be compared



Cyclic Voltammetry of [$Ru(CH_2C_6H_4CH_2)(PPh_2Me)_3$] in 0.1 M Bu_4NPF_6 / CH_2Cl_2 medium at 200 mVs^{-1}

Figure 2.53

with results obtained by Dixneuf in his studies on iron o-xylidenes [51]. An irreversible wave is also observed and can be attributed to a Ru (I) / Ru (III) couple which may decompose with phosphine dissociation. The ease of the first oxidation of [$Ru(CH_2C_6H_4CH_2)P_3$] confirms their electron-rich character. The lowering of the corresponding potential follows the expected increase in electron-donor ability of the phosphine ligands with $PMe_3 > PPh_2Me$.

2.14 Experimental

Microanalyses were carried out by St. Andrews University laboratories. N.m.r spectra were recorded on Bruker WP-80, AM-300, and Varian CFT-20 spectrometers. All manipulations were carried out using standard Schlenk-line and catheter tubing techniques. All solvents were carefully dried before use by a) distillation from sodium diphenylketone, (diethyl ether, toluene and light petroleum ether (boiling range 40 - 60°C)), b) distillation from calcium hydride, (dichloromethane), or c) distillation from magnesium methoxide, (methanol).

O-xylene (Aldrich), 1,2,3-trimethylbenzene (Aldrich), and 1,2,3,4-tetramethylbenzene (Aldrich) were distilled and stored over sodium wire prior to use. 1,2,4,5-tetramethylbenzene (Aldrich) was recrystallized from ethanol. Dichlorophenylphosphine (Lancaster) and chlorodiphenylphosphine (Lancaster), were purified by

vacuum distillation and stored under an atmosphere of dinitrogen. Tetramethylethylenediamine (Aldrich), was purified by distillation in an atmosphere of dinitrogen, and stored under dinitrogen. Triphenylphosphine (Fluka), 2,3-dimethylnaphthalene (Fluka) and 1,2-dimethylnaphthalene (Fluka) were used as received without further purification.

The compounds trimethylphosphine [102], dimethylphenylphosphine [103,104], methyldiphenylphosphine [103,104], [$RuCl_2(PPh_3)_3$] [96], [$RuCl_2(PMe_2Ph)_4$] [92,105], [$RuCl_2(PPh_2Me)_4$] [105], [$RuCl_2(PMe_3)_4$] [106,107], [$RuCl_2(P(OPh)_3)_4$] [100], [$RuHCl(PPh_3)_3$] [108], were prepared by standard literature methods.

Preparation of lithium reagents

To a stirred solution of butyllithium in hexane (6 cm^3, 9.6 x 10^{-3} mol, 1.6 M) cooled to 0°C was added TMEDA (3.0 cm^3, 19.8 x 10^{-3} mol). After 15 mins the appropriate dimethylbenzene (10 x 10^{-3} mol) in petroleum ether (40 cm^3) was added and the mixture stirred for a further 15 mins before removing the ice-bath and allowing the mixture to react for 24 h. Where possible the petroleum ether was removed by filtration and the lithium salt dissolved in diethyl ether (40 cm^3). After titration the lithium reagent was ready for use.

Tris(methyldiphenylphosphine)(1-α,2-α':η^4-quinodimethan e) ruthenium(0)

a) The complex [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028×10^{-3} mol) was stirred with a solution of 1-lithiomethyl-2-methylbenzene.TMEDA (2.5×10^{-3} mol). After 24 h , water (20 cm^3) was added to the deep orange solution and after shaking vigorously and allowing to settle , the ethereal layer was decanted and dried over anhydrous magnesium sulphate. The diethyl ether was removed in vacuo. Excess o-xylene and liberated methyldiphenylphosphine were removed by sublimation in vacuo at 120°C onto a cold-finger (-78°C). The resulting dark orange gum was dissolved into toluene. After filtration , concentration and the addition of light petroleum ether , the product separated as orange crystals which were collected and dried in vacuo. Yield 0.40 g (48 %).

b) The complex [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028×10^{-3} mol) was stirred with a solution of the di-Grignard , [o-$C_6H_4(CH_2MgCl)_2$] , (50 cm^3 , 2.5×10^{-3} mol).The solution was stirred for 24 h and the solvent removed in vacuo. The residue was extracted with diethyl ether and after work-up (see above) , orange crystals were obtained. Yield 0.47 g (57 %). ^1H n.m.r (benzene-d_6 , 300 MHz 298 K) : δ 7.84 - 6.55 (complex , aromatic) ; δ 2.22 (d , $^2J_{PH}$ =

7.01 Hz , P_AMe) ; δ 1.99 (pdd , $^2J_{HH}$ = 3.93 Hz , $^3J_{PH}$ = 5.86 Hz , H_B) ; δ 1.69 (pd , $^2J_{PH} + {}^4J_{PH}$ = 4.34 Hz , P_BMe) ; δ 0.68 (pdd , $^2J_{HH}$ = 3.93 Hz , $^3J_{PH}$ = 6.86 Hz , H_A). ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 36.03 (s , $P_A Ph_2$Me) ; δ 20.42 (s , $P_B Ph_2$Me). Found : C , 71.02 ; H , 5.74. $C_{47}H_{47}P_3Ru$ requires : C , 70.05 ; H , 5.88.

The following complexes were similarly prepared , but with the work-up after washing with water as described.

Tris(trimethylphosphine)(1-α,2-α':η^4-quinodimethane) ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55 g , 1.155 x 10^{-3} mol) and 1-lithiomethyl-2-methylbenzene.TMEDA (3.0 x 10^{-3} mol). The diethyl ether was removed in vacuo. Excess o-xylene was removed in vacuo at 80°C. The orange gum was dissolved in light petroleum ether. After , filtration , concentration and cooling to -30°C , the product separated as orange crystals , which were collected and dried in vacuo. Yield 0.20 g (40 %). ^{1}H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.53 - 7.10 (AA'BB' , 4 H) ; δ 1.96 (pdd , $^2J_{HH}$ = 3.72 Hz , $^3J_{PH}$ = 5.62 Hz , H_B) ; δ 1.42 (d ,

$^2J_{PH}$ = 7.92 Hz , P_AMe) ; δ 1.03 (pd , $^2J_{PH}$ + $^4J_{PH}$ = 5.87 Hz , P_BMe) ; δ - 0.04 (pdd , $^2J_{HH}$ = 3.72 Hz , $^3J_{PH}$ = 6.56 Hz , H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 14.87 (t , $^2J_{PP}$ = 8.72 Hz , P_AMe_3) ; δ -8.38 (d , $^2J_{PP}$ = 8.72 Hz , P_BMe_3). ^{13}C-{^1H} n.m.r (benzene-d_6 , 75.47 MHz , 298 K) : δ 131.65 (s , C5,C8) ; δ 122.97 (s , C6,C7) ; δ 101.65 (s , C2,C3) ; δ 29.70 (m , $^2J_{PC}$ = 37.39 Hz , $^2J_{PC}$ = 4.30 Hz , $^2J_{PC}$ = 5.00 Hz , C1,C4) ; δ 25.06 (dt , $^1J_{PC}$ = 23.4 Hz , $^3J_{PC}$ = 3.0 Hz , P_ACH_3) ; δ 22.76 (m , $^1J_{PC}$ = 19.95 Hz , $^3J_{PC}$ = 2.35 Hz , P_BCH_3). Found : C , 47.43 ; H , 8.66. $C_{17}H_{35}P_3Ru$ requires : C , 47.11; H, 8.14.

Tris(methyldiphenylphosphine)(1-α,2-α':η⁴-4,5-dimethylquinodimethane)ruthenium(0)

From [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028 x 10^{-3} mol) and 1-lithiomethyl-2,4,5-trimethylbenzene.TMEDA (2.5 x 10^{-3} mol). The diethyl ether was removed in vacuo. Excess durene and liberated methyldiphenylphosphine were removed by sublimation in vacuo at 120°C onto a cold finger (-78°C). The resulting orange gum was dissolved into 80 -100 petroleum ether. After filtration and concentration the product separated as a yellow-orange powder which was collected and dried in vacuo. Yield 0.27 g (31

%). ^1H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.83 - 6.70 (complex , aromatic) ; δ 2.24 (d , $^2J_{PH}$ = 6.97 Hz , P_AMe) ; δ 2.22 (s , CH_3) ; δ 1.96 (pdd , $^2J_{HH}$ = 3.44 , $^3J_{PH}$ = 6.13 Hz , H_B) ; δ 1.73 (pd , $^2J_{PH} + {}^4J_{PH}$ = 4.37 Hz , P_BMe) ; δ 0.73 (pdd , $^2J_{HH}$ = 3.44 Hz , $^3J_{PH}$ = 7.08 Hz , H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 35.18 (s , P_APh_2Me) ; δ 21.45 (s , P_BPh_2Me). Found : C , 69.25 ; H , 6.12. $C_{49}H_{51}P_3Ru$ requires : C , 70.57 ; H , 6.16.

Tris(trimethylphosphine)(1-α,2-α':η⁴-4,5-dimethylquinodimethane)ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55 g , 1.155 x 10^{-3} mol) and 1-lithiomethyl-2,4,5-trimethylbenzene.TMEDA (3.0 x 10^{-3} mol). The diethyl ether was removed in vacuo. Excess durene was removed by sublimation in vacuo at 100°C onto a cold-finger (-78°C). The resulting yellow gum was dissolved into light petroleum ether. After filtration , concentration and cooling to -30°C , the product separated as yellow crystals , which were collected and dried in vacuo. Yield 0.19 g , (36 %). ^1H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.22 (s , 2 H) ; δ 2.28 (s ,

CH_3) ; δ 1.95 (pdd , $^2J_{HH}$ = 3.52 Hz , $^3J_{PH}$ = 5.58 Hz , H_B) ; δ 1.45 (d , $^2J_{PH}$ = 7.34 Hz , P_AMe) ; δ 1.03 (pd , $^2J_{PH} + {}^4J_{PH}$ = 5.28 Hz , P_BMe) ; δ 0.00 (pdd , $^2J_{HH}$ = 3.52 Hz , $^3J_{PH}$ = 7.04 Hz , H_A). ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 13.97 (t , $^2J_{PP}$ = 7.27 Hz , P_AMe$_3$) ; δ -5.46 (d , $^2J_{PP}$ = 7.27 Hz , P_BMe$_3$). Found : C , 50.85 ; H , 8.85. $C_{19}H_{39}P_3Ru$ requires : C , 49.45 ; H , 8.52.

Tris(methyldiphenylphosphine)(1-α,2-α':η^4-3-methylquino dimethane)ruthenium(0)

From [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028 x 10^{-3} mol) and the lithium salt of 1,2,3-trimethylbenzene (2.5 x 10^{-3} mol). The diethyl ether was removed in vacuo. Excess 1,2,3-trimethylbenzene and liberated methyldiphenylphosphine were removed by sublimation in vacuo at 120°C onto a cold-finger (-78°C). The resulting orange gum was dissolved into toluene. After filtration and concentration the product separated as orange crystals , which were collected and dried in vacuo. Yield 0.41 g , (49 %). ^{1}H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.80 - 6.55 (complex , aromatic) ; δ 2.33 (bm , H_B) ; δ 2.28 (d , $^2J_{PH}$ = 7.10 Hz , P_AMe) ; δ 2.22 (s , CH_3) ; δ 1.98 (bm , $H_{B'}$) ; δ

1.71 (d , $^2J_{PH}$ = 5.17 Hz , P_BMe) ; δ 1.51 (d , $^2J_{PH}$ = 5.24 Hz , P_CMe) ; δ 0.64 (bm , $H_{A'}$) ; δ 0.27 (bm , H_A). ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 35.82 (s , P_APh_2Me) ; δ 17.87 (d , $^2J_{PP}$ = 22.51 Hz , P_BPh_2Me) ; δ 16.40 (d , $^2J_{PP}$ = 22.51 Hz , P_CPh_2Me). Found : C , 71.42 ; H , 6.26. $C_{48}H_{49}P_3Ru$ requires : C , 70.32 ; H , 6.06.

Tris(trimethylphosphine)(1-α,2-α':η^4-3-methylquinodimethane)ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55 g , 1.155 x 10^{-3} mol) and the lithium salt of 1,2,3-trimethylbenzene (3.0 x 10^{-3} mol). The diethyl ether was removed in vacuo. Excess 1,2,3-trimethylbenzene was removed by sublimation in vacuo at 100°C onto a cold finger (-78°C). The resulting yellow oil was dissolved in light petroleum ether. After filtration , concentration and cooling to -30°C , the product separated as yellow crystals , which were collected and dried in vacuo. Yield 0.21 g , (41 %). ^{1}H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.44 - 6.98 (m , 3 H) ; δ 2.27 (s , CH_3) ; δ 2.17 (bm , H_B) ; δ 1.91 (bm , $H_{B'}$) ; δ 1.44 (d , $^2J_{PH}$ = 7.81 Hz , P_AMe) ; δ 1.07 (d , $^2J_{PH}$ = 6.10 Hz , P_BMe) ; δ 1.04 (d , $^2J_{PH}$ = 6.10 Hz ,

$P_C Me$) ; δ - 0.16 (bm , $H_{A'}$) ; δ - 0.22 (bm , H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 14.25 (pt , $^2J_{PP} + {}^2J_{PP}$ = 16.85 Hz , $P_A Me_3$) ; δ -7.60 (dd , $^2J_{PP}$ = 8.48 Hz , $^2J_{PP}$ = 29.46 Hz , $P_B Me_3$) ; δ -11.25 (dd , $^2J_{PP}$ = 8.37 Hz , $^2J_{PP}$ = 29.46 Hz , $P_C Me_3$). Found : C , 49.01 ; H , 8.67. $C_{18}H_{37}P_3Ru$ requires : C , 48.32 ; H , 8.33.

Tris(trimethylphosphine)(1-α,2-α':η⁴-3,4-dimethylquinodi methane)ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55g , 1.155×10^{-3} mol) and the lithium salt of 1,2,3,4-tetramethylbenzene (3.0×10^{-3} mol). The diethyl ether was removed in vacuo. Excess 1,2,3,4- tetramethyl-benzene was removed by sublimation in vacuo at 120°C onto a cold-finger (-78°C). The resulting yellow oil was examined by ^{31}P n.m.r and shown to contain both the title compound and tris(trimethylphosphine)(1-α,2-α':η⁴-3,6-dimethylquinodimethane)r uthenium(0) , (82) , in the approximate ratio 2 : 1. ^{31}P-{^1H} n.m.r of (82) , (benzene-d_6 , 120.81 MHz , 298 K) : δ 14.25 (t , $^2J_{PP}$ = 7.92 Hz , P_A) ; δ - 10.85 (d , $^2J_{PP}$ = 7.92 Hz , P_B). The yellow oil was dissolved into light petroleum ether. After filtration ,

concentration , and cooling to -30°C , the title product separated as yellow crystals which were collected and dried in vacuo. Yield 0.12 g (23%). ^1H n.m.r (benzene-d_6 , 80 MHz , 298 K) : δ 7.44 - 6.84 (AB , 2H) ; δ 2.40 (s , CH_3) ; δ 2.28 (s ,CH_3) ; δ 2.21 (bm , H_B) ; δ 1.88 (bm , $H_{B'}$) ; δ 1.42 (d , $^2J_{PH}$ = 7.8 Hz , P_AMe) ; δ 1.03 (d , $^2J_{PH}$ = 5.8 Hz , P_BMe) ; δ 0.95 (d , $^2J_{PH}$ = 6.0 Hz , P_CMe) ; δ - 0.23 (bm , $H_{A'}$ and H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 ,120.81 MHz , 298 K) : δ 14.78 (pt , $^2J_{PP}$ = 7.36 Hz , $^2J_{PP}$ = 8.01 Hz , P_A) ; δ - 7.62 (aq , $^2J_{PP}$ = 7.36 Hz , $^2J_{PP}$ = 29.13 Hz , P_B) ; δ - 7.89 (aq , $^2J_{PP}$ = 8.01 Hz , $^2J_{PP}$ = 29.13 Hz , P_C). Found : C , 49.67 ; H , 8.83 . $C_{19}H_{39}P_3Ru$ requires : C , 49.45 ; H , 8.52.

[$RuH(C_6H_4OP(OPh)_2)(P(OPh)_3)_3$]

From [$RuCl_2(P(OPh)_3)_4$] (1.412g , 1.0 x 10^{-3} mol) and 1-lithiomethyl-2-methylbenzene.TMEDA (2.5 x 10^{-3} mol). The diethyl ether was removed in vacuo. The pale-orange oil was dissolved into toluene. After filtration and addition of light petroleum ether a grey-white powder was obtained. Recrystallization from toluene yielded a white crystalline solid which was collected and dried in vacuo. Yield 0.83 g , (62 %).

I.R ν (Ru-H) 1910 cm^{-1}. ^{1}H n.m.r (benzene-d_6, 300 MHz , 298 K) : δ 8.82 - 6.68 (complex , aromatic) ; δ 2.3 (s , toluene of crystallization) ; δ -7.8 (pdq , $^{2}J_{PH}$ = 129.79 Hz , $^{2}J_{PH}$ = 21.65 Hz , $^{2}J_{PH}$ = 25.79 Hz , $^{2}J_{PH}$ = 21.95 Hz , Ru-H). ^{31}P-{^{1}H} n.m.r (benzene-d_6, 120.81 MHz , 298 K) : δ 163.28 (pddd , $^{2}J_{PP}$ = 641.95 Hz , $^{2}J_{PP}$ = 57.91 Hz , $^{2}J_{PP}$ = 39.09 Hz , P_A) ; δ 138.96 (pq , $^{2}J_{PP}$ = 57.91 Hz , $^{2}J_{PP}$ = 49.06 Hz , $^{2}J_{PP}$ = 46.16 Hz , P_B) ; δ 138.38 (pddd , $^{2}J_{PP}$ = 641.95 Hz , $^{2}J_{PP}$ = 49.06 Hz , $^{2}J_{PP}$ = 46.25 Hz , P_C) ; δ 126.69 (m , $^{2}J_{PP}$ = 39.09 Hz , $^{2}J_{PP}$ = 46.29 Hz , $^{2}J_{PP}$ = 46.16 Hz , P_D). Found : C , 66.23 ; H , 4.73. $C_{72}H_{60}O_4P_4Ru.C_6H_5CH_3$ requires : C , 66.15 ; H , 4.78.

CHAPTER THREE

O-NAPHTHOQUINODIMETHANE COMPLEXES OF RUTHENIUM(0)

3.1 Introduction

The object of much of the work described in chapter 2 has been to develop a general synthesis of ruthenium complexes containing a substituted o-xylidene ligand bound as an o-quinodimethane.

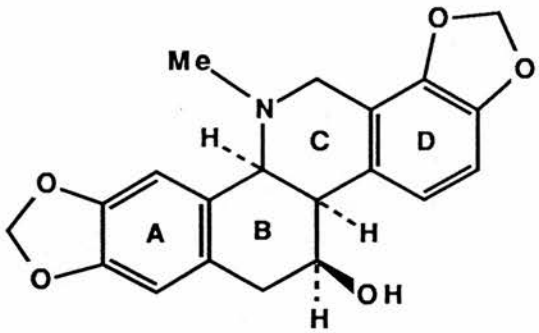
As stressed earlier, o-quinodimethanes have been recognised as important intermediates in the synthesis of natural products.

In the synthesis of Chelidonine [109], (**90**), (figure 3.1), the key step is the heating of (**91**), which is essentially a substituted o-quinodimethane, to give the internal Diels-Alder adduct, (**92**), in high yield.

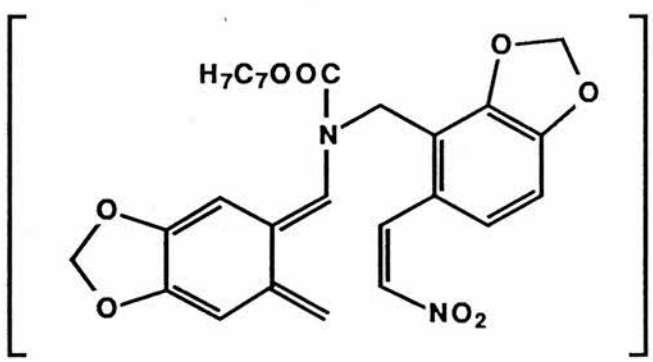
Many syntheses of natural products however, involve polycyclic ring systems, and much of the framework of these ring systems is already established before the participation of the o-quinodimethane.

The synthesis of 4-demethoxydaunomycinone [110], (**93**), involves the construction of ring A by the Diels-Alder addition of a reactive o-quinodimethane intermediate, (**94**) to the olefinic portion of an α,β-unsaturated ketone, (figure 3.2).

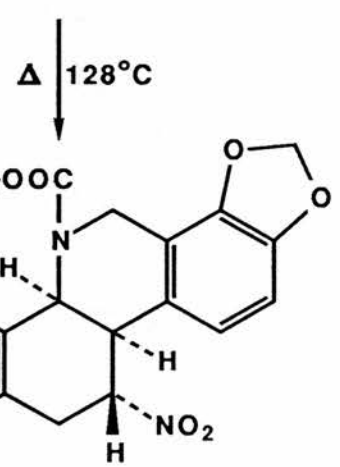
Clearly the advantages of being able to construct complexes of ruthenium in which the metal is bound in an η^4-manner as with o-quinodimethane, but in which the ligand contains a polycyclic ring system, rather than a single ring, are obvious.



Chelidonine (90)

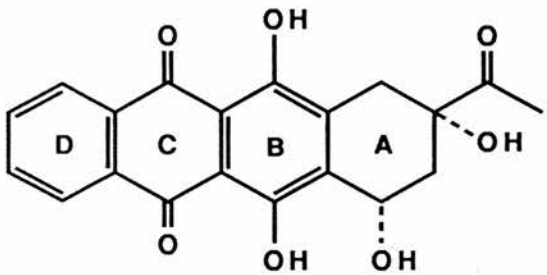


(91)

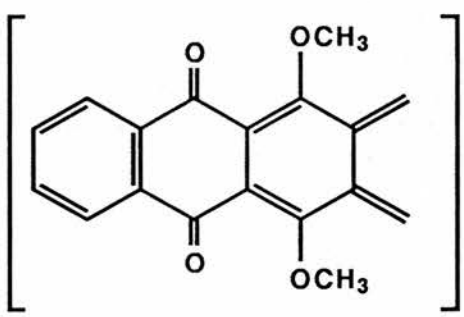


(92)

Figure 3.1



4-demethoxydaunomycinone (93)



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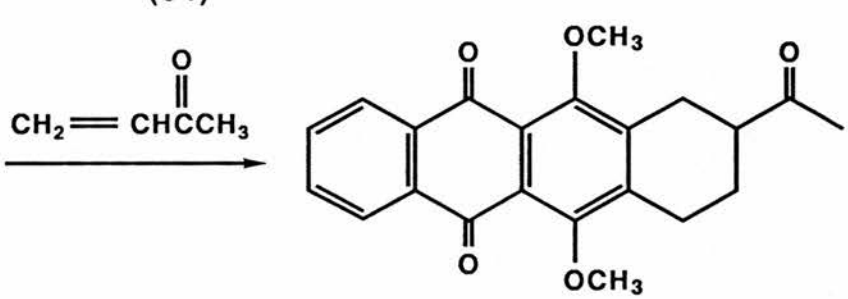
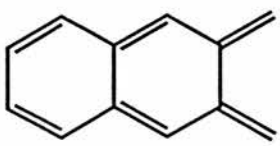


Figure 3.2

This chapter will describe the synthesis of naphthoquinodimethane complexes of ruthenium. A discussion of further mechanistic findings will also be given.

3.2 O-naphthoquinodimethanes

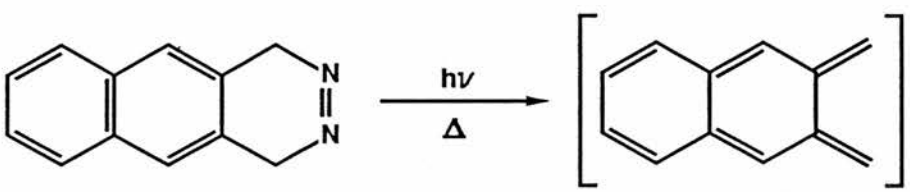
Matrix-isolated 2,3-naphthoquinodimethane, (**95**) , (figure 3.3) , has been obtained previously by photolysis of



2,3-naphthoquinodimethane (95)

Figure 3.3

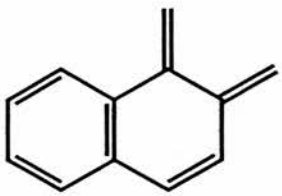
1,4-dihydrobenzo[g]-phthalazine [111] , (**96**) , (figure 3.4). The electronic structure of its ground state has been discussed.



(96)

Figure 3.4

1,2-naphthoquinodimethane , (**97**) , (figures 3.5 and 3.6) has also been detected by a technique of flow ^{1}H n.m.r [112]. The flow technique provides a useful complement to the matrix-isolation technique which allows UV-visible, I.R, and electronic measurements to be made on short-lived species.



1,2-naphthoquinodimethane (97)

Figure 3.5

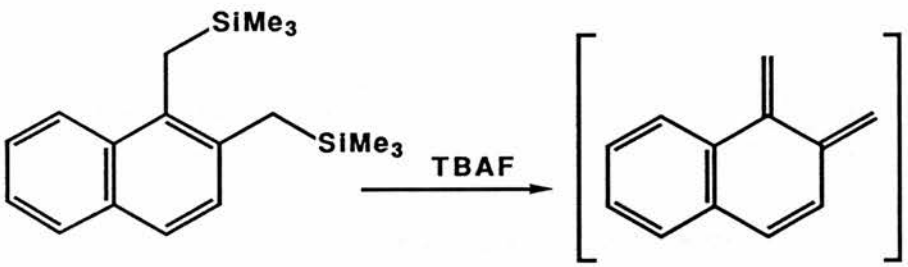


Figure 3.6

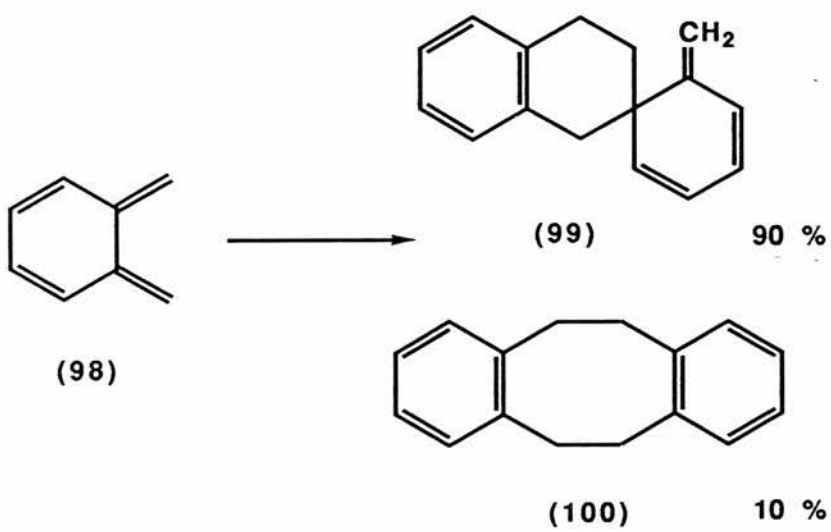
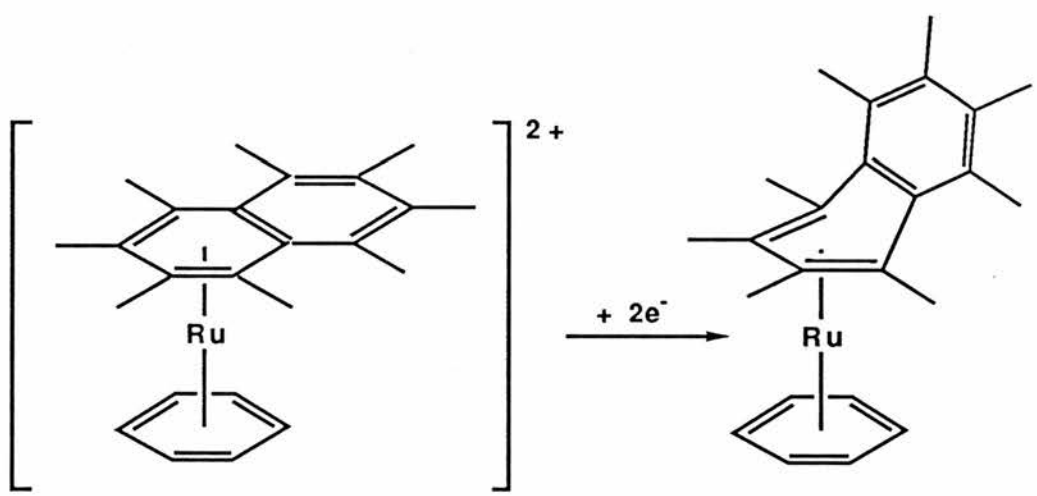


Figure 3.7

It is interesting to note that (**97**) has been shown to be ca. 100 times less reactive towards dimerization than o-quinodimethane, (**98**). In fact using the same flow n.m.r techniques , (**98**) , could not be detected without the presence of its dimers , (**99**) and (**100**) , (figure 3.7).

3.3 Tetrahapto binding of naphthalene ring systems

Tetrahapto binding has been seen previously in naphthalene complexes of ruthenium. Hull and Gladfelter[113] have prepared

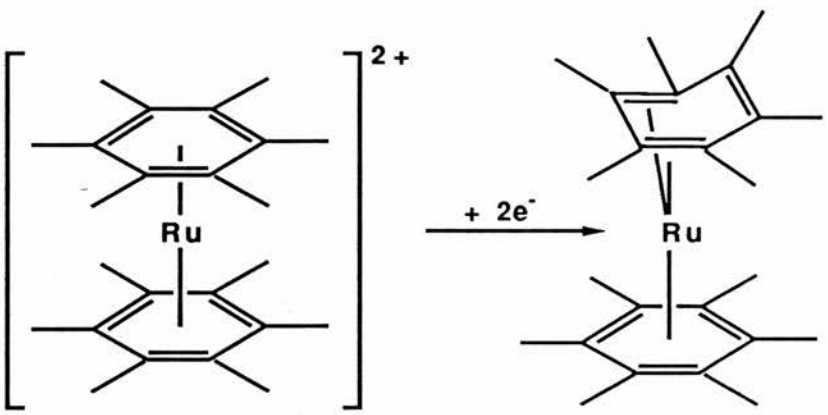


(101) **(102)**

Figure 3.8

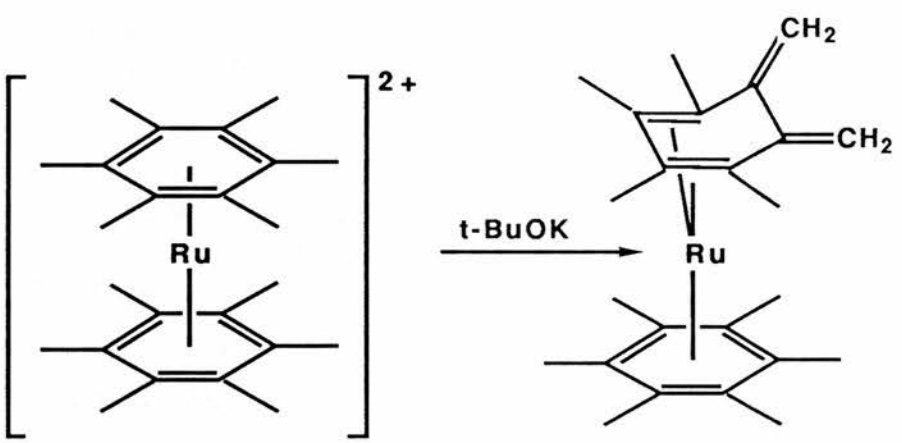
[Ru(OMN)(arene)] (OMN = octamethylnaphthalene , arene =

p-cymene , mesitylene , prehnitene and C_6Me_6) complexes , in which the OMN ligand binds as an η^4-ligand (**102**) , by a



(103) (104)

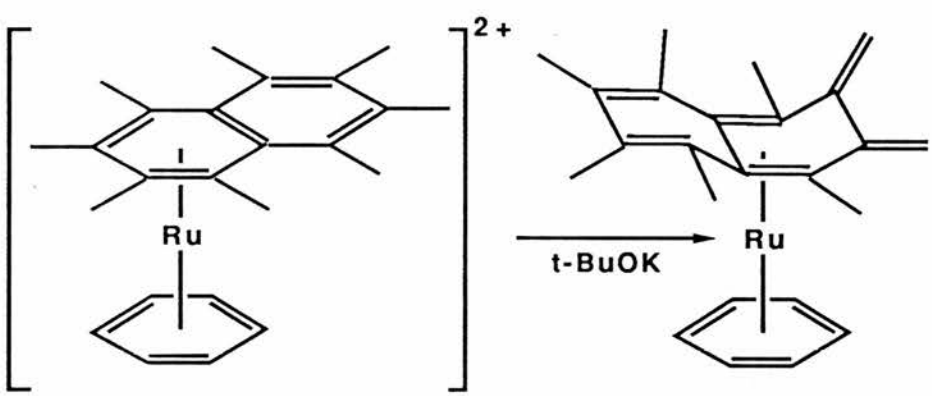
Figure 3.9



(105)

Figure 3.10

two-electron reduction of the dications [Ru(OMN)(arene)]$^{2+}$, (**101**) , with sodium amalgam , (figure 3.8). The reaction is analogous to that reported by Fischer and Elschenbroich [114] in 1970 which was one of the premier examples of η^4-binding. The dication [$Ru(C_6Me_6)_2$]$^{2+}$, (**103**) , underwent a two-electron reduction and caused one of the ligands to bind as an η^4-C_6Me_6 , (**104**) , (figure 3.9). As mentioned previously in chapter 1 , Gladfelter [49] has also shown that a double deprotonation of the precursor [$Ru(C_6Me_6)_2$]$^{2+}$, used by Fischer and Elschenbroich , with potassium tert-butoxide results in the formation of an o-quinodimethane complex , in which the unusual η^4-binding of the metal to the endocyclic diene can be



(106)

Figure 3.11

seen , (**105**) , (figure 3.10). One can envisage from this result that a double deprotonation of the precursor [Ru(OMN)(arene)]$^{2+}$ with potassium tert-butoxide might result in a complex in which η^4-endocyclic binding to a naphthoquinodimethane ligand will occur , (**106**) , (figure 3.11).

It appears however that this has not been attempted.

In contrast deprotonation of o-dimethylnaphthalenes with BuLi.TMEDA and further reaction with [$RuCl_2P_4$] (P = PMe_3 , PMe_2Ph , or PPh_2Me) results in complexes which can be shown to contain an o-naphthoquinodimethane ligand bound in an η^4-fashion to the exocyclic double bonds of the ligand. Although crystals of these complexes have been obtained , in almost all cases they have not been suitable for X-ray structural analysis. The identification therefore relies on spectroscopic data and comparison with the spectral data of the o-quinodimethane complexes.

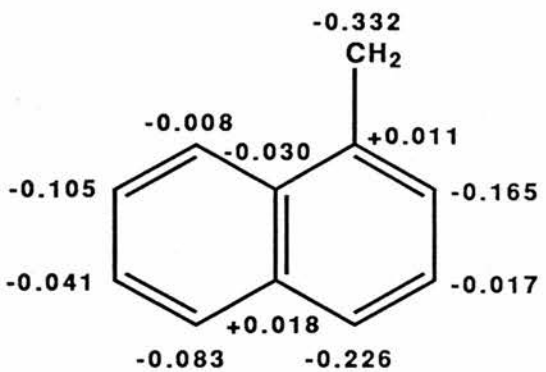
The isolation of these o-naphthoquinodimethane complexes is somewhat surprising since η^4-binding leads to localization of the bonding in the aromatic system. Assuming that this occurs in the naphthoquinodimethane complexes a much larger resonance energy will be lost than for the o-quinodimethane complexes. This demonstrates the very high affinity of ruthenium for diene-like coordination.

3.4 Metallation of polymethylnaphthalenes

A reasonable explanation for the relative reactivities of the isomeric xylenes and dimethylnaphthalenes has been offered [115] based primarily on the assumption that the second hydrogen is the more difficult one to remove and that therefore in most cases mono-metallation predominates. The relative ease of removal of a particular second hydrogen will depend upon the charge density at various positions in the monoanion. For example since the negative charge in the benzylanion is delocalized into the ring positions in the order para > ortho > meta [116] the observed reverse order for dimetallation of the xylenes (meta > ortho > para) is easily rationalized.

Work by Dunkelblum and Hart [117] has shown that despite a substantial excess of metallating agent (BuLi.TMEDA) the exclusive or predominant reaction when metallating polymethylnaphthalenes is the mono-metallated product.

A surprising result was the metallation of the C2 methyl group in preference to the C1 methyl. Calculations on the 1-naphthyl , (**107**) , and 2-naphthyl carbanions , (**108**) , (figure 3.12) [118] and simple resonance theory have predicted that the negative charge should be more dispersed in the former, leading one to expect metallation at the C1 methyl to be preferred.



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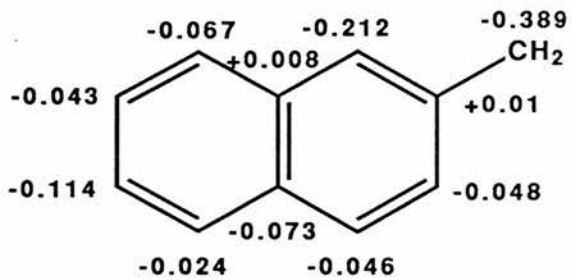


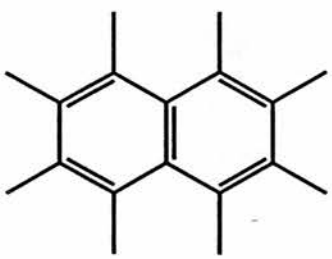
(108)

Figure 3.12

The calculations shown for the 1- and 2-naphthyl carbanions assumed a planar geometry.

It is thought that the coplanarity of the methyl substituents and the aromatic ring might be important. The C2 methyls are closer to coplanarity with the naphthalene ring than are the C1 methyls. In (**109**) , (figure 3.13) , for example , the angle between the C1 and C2 methyls and the mean molecular plane is 20° and 10° respectively [119]. In polymethylnaphthalenes the possibility for charge dispersion in the C1 carbanion will be

diminished relative to that of the C2 carbanion as a consequence of this molecular distortion.



(109)

Figure 3.13

Further the BuLi.TMEDA which is a rather large base may attack the C2 methyl to avoid the large steric interactions at the peri positions.

3.5 Preparation of o-naphthoquinodimethane complexes of ruthenium

Reaction of a two to three - fold excess of 2-lithiomethyl-3-methylnaphthalene.TMEDA with [$RuCl_2P_4$] (P = PPh_2Me or PMe_3), or of a similar excess of the lithium salt of 1,2-dimethylnaphthalene with [$RuCl_2P_4$] (P = PPh_2Me , PMe_2Ph or PMe_3), in diethyl ether, leads to orange solutions for the 1,2-dimethylnaphthalene reactions, and red solutions for the 2,3-dimethylnaphthalene reactions from which compounds

analyzing as [$Ru(CH_2C_{10}H_6CH_2)P_3$] , (figure 3.14) , may be isolated in reasonable yield.

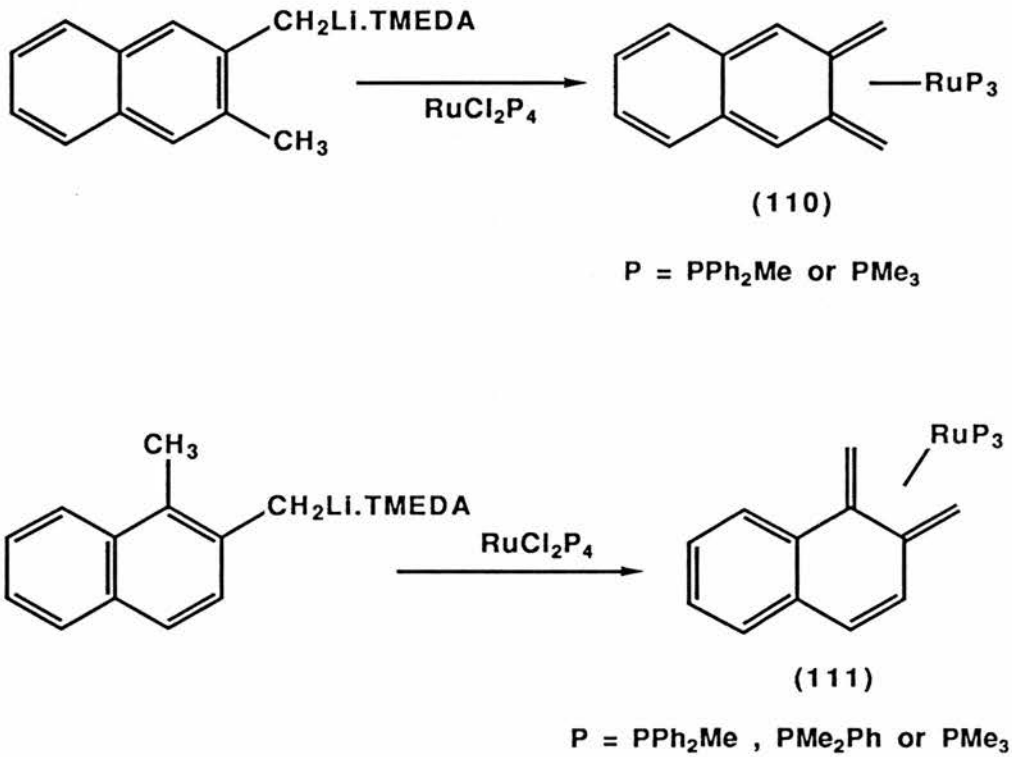


Figure 3.14

Somewhat surprisingly the expected naphthoquinodimethane was not obtained from reaction of [$RuCl_2(PMe_2Ph)_4$] with 2-lithiomethyl-3-methylnaphthalene.TMEDA , but instead the major product would appear from spectroscopic studies to contain an intact ($CH_2C_{10}H_6CH_3$) group bound in an η^3 - allyl fashion . The ^1H n.m.r spectrum is similar to that of the η^3 - bound

o-methylbenzyl ligand in [$Rh(o\text{-}CH_2C_6H_4CH_3)(PPh_3)_2$] [120] although the multiplicities suggest more coupling to phosphorus. This result cannot be confirmed however due to difficulties in isolation of the compound.

3.6 Spectroscopic properties

The ^1H n.m.r and ^{31}P n.m.r spectra (figures 3.15 and 3.16) of the 2,3-naphthoquinodimethane complexes are very similar to those of their o-quinodimethane analogues with doublets of doublets being observed near δ 0 and δ 2 for the endo and exo methylene hydrogens , respectively , pseudodoublets with some intensity between the outer lines arising from the $A_nXX'A'_n$ spin system of the methyl groups of the two symmetry related phosphines , and a doublet from the methyl group(s) of the unique phosphine. For [$Ru(CH_2C_{10}H_6CH_2)(PMe_3)_3$] , the resonances from the aromatic hydrogens confirm that a plane of symmetry runs through the naphthalene ring. As for the related o-quinodimethane complexes , $^2J_{PP}$ in the ^{31}P n.m.r spectrum is small (< 11 Hz) confirming that the P - Ru - P angle is close to 100°. The rather larger value observed for the PMe_3 complex than for the bulkier phosphine suggests , as for the o-xylidene complexes , a slightly smaller angle on account of reduced steric interaction.

Figure 3.15 Selected ^1H n.m.r data for the new naphthoquinodimethane complexes [a]

Compound	P_AMe (J_{PH})	P_BMe (J_{PH})	P_CMe (J_{PH})	CH_{exo} (J_{PH})	CH_{endo} (J_{PH})	(J_{HH})
[$Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PPh_2Me)_3$]	2.16 d(7.8)	1.50 pd(4.1)[b]		1.74 dd(5.5)	0.73 dd(4.5)	4.5
[$Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3$]	1.42 d(8.1)	0.94 pd(5.8)[b]		2.26 dd(8.0)	0.49 dd(6.2)	4.5
[$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PPh_2Me)_3$]	2.28 d(6.8)	1.55 d(5.8)	1.35 d(5.7)	2.55 m , 2.04 m	0.38 m , [2H]	
[$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_2Ph)_3$]	1.75 d(7.0)	1.15 d(5.8) 1.03 d(6.0)	0.99 d(5.7) 0.95 d(6.0)	2.53 m , 2.16 m	- 0.45 m , [2H]	
[$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3$]	1.46 d(8.1)	1.01 d(6.1)	0.64 d(6.0)	2.65 m , 1.98 m	- 0.07 m , - 0.32 m	

[a] Chemical shifts in ppm to high frequency of $SiMe_4$, coupling constants in Hz ; measured in C_6D_6 at 298K using C_6D_5H (δ 7.27) as internal reference ; s = singlet , d = doublet , t = triplet , m = multiplet , p = pseudo.

[b] $J_{PH} + J_{PH'}$

Figure 3.16 ^{31}P n.m.r data for the new naphthoquinodimethane complexes

Compound	Chemical Shifts [a]			Coupling Constants (J , Hz)		
	P_A	P_B	P_C	P_AP_B	P_AP_C	P_BP_C
[Ru(2,3-$CH_2C_{10}H_6CH_2$)(PPh_2Me)$_3$]	41.4 (t)	19.5 (d)		4.0	4.0	-
[Ru(2,3-$CH_2C_{10}H_6CH_2$)(PMe_3)$_3$]	28.5 (t)	0.2 (d)		10.7	10.7	-
[Ru(1,2-$CH_2C_{10}H_6CH_2$)(PPh_2Me)$_3$]	30.2 (s)	20.3 (d)	15.6 (d)	< 2	< 2	24.2
[Ru(1,2-$CH_2C_{10}H_6CH_2$)(PMe_2Ph)$_3$]	20.1 (t)	4.1 (dd)	2.7 (dd)	3.5	3.7	29.6
[Ru(1,2-$CH_2C_{10}H_6CH_2$)(PMe_3)$_3$]	8.0 (t)	- 6.3 (dd)	- 9.8 (dd)	7.7	8.0	32.3

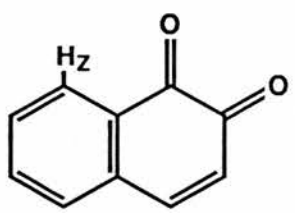
[a] Chemical shifts in ppm to high frequency of external 85% H_3PO_4 , measured in C_6D_6 at 298K.

For the 1,2-naphthoquinodimethane complexes the lack of a plane of symmetry in the molecules means that more complex spectra are observed with separate doublets from the methyl groups on each phosphine , and separate resonances , showing coupling to several nuclei , for the methylene hydrogens . The spectra are somewhat similar to those obtained for the methylquinodimethane complexes , [$Ru(CH_2C_6H_3\{CH_3\}CH_2)P_3$]. For P = Me_2Ph , six doublet resonances were observed from the methyl groups , since each pair is diastereotopic (no plane of symmetry runs through any of the phosphorus atoms). In the ^{31}P n.m.r spectra separate resonances are observed for each phosphorus atom. Coupling constants are again comparable with their o-quinodimethane analogues.

Whilst X-ray studies have shown that there is significant bond localization in the o-quinodimethane complex of [$Ru(CH_2C_6H_4CH_2)(PMe_2Ph)_3$] , none of the naphthoquinodimethane complexes have given crystals of sufficient quality for X-ray structure determination. Consequently a direct indication of the extent of bond localization is not possible.

^1H n.m.r studies do show however that the phenyl region for [$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3$] in which $\eta^2 : \eta^2$ bonding occurs , is quite different from the phenyl region of the parent 1,2-dimethylnaphthalene with one distinct hydrogen resonating at low field (δ 8.35). The phenyl region of this compound is

similar to that of 1,2-naphthoquinone , (**112**) , (figure 3.17) , (low field resonance at δ 8.05) [121] in which the bonding is forced to be as in the localized bonding picture.



(112)

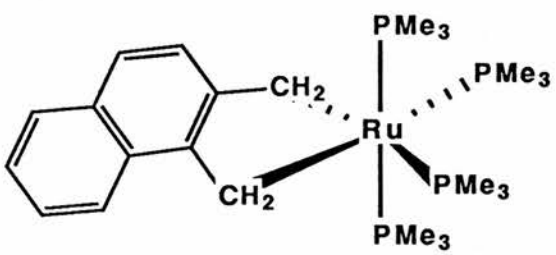
Figure 3.17

The low field resonance arises from the hydrogen (H_z) . It can therefore be concluded that significant bond localization does occur at least for the 1,2-naphthoquinodimethane complexes.

The U.V spectrum of [$Ru(2,3\text{-}CH_2C_{10}H_6CH_2)(PPh_2Me)_3$] shows strong absorptions near 510 n.m , which accounts for the dark red colour of the complex. The absorption is close to the position of the major absorption observed for matrix isolated 2,3-naphthoquinodimethane [111] , (541 n.m) , which is also reported to be red and suggests that significant bond localization also occurs in the 2,3-naphthoquinodimethane complexes.

Although the major product isolated from the reaction of

[$RuCl_2(PMe_3)_4$] with the lithium salt of 1,2-dimethylnaphthalene was the expected 1,2-naphthoquinodimethane , a second product was also isolated. This was originally postulated as [$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_4$] (**113**) , (figure 3.18) , in which the ligand is bound as a σ-metallacycle , a situation similar to that seen many times in chapter one.

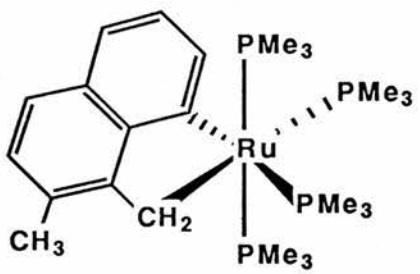


(113)

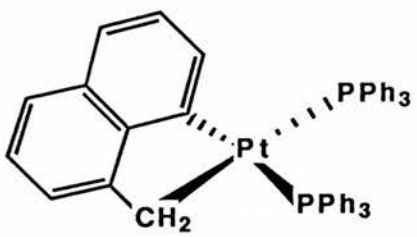
Figure 3.18

Although this had been recognized as a possible product due to the reluctance of [$RuCl_2(PMe_3)_4$] to lose a phosphine , it was difficult to understand why a similar product was not observed from the reaction of 2-lithiomethyl-3-methylnaphthalene.TMEDA and [$RuCl_2(PMe_3)_4$] .

Further purification and spectral analysis of the complex has now shown it to be [$Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4$] , (**114**) , (figure 3.19) , a compound similar to the platinum compound , [$Pt(C_{10}H_6CH_2)(PPh_3)_2$] , (**115**) , prepared by Shaw [55].



(114)



(115)

Figure 3.19

^{31}P n.m.r

The ^{31}P n.m.r spectrum , (figures 3.20 and 3.21) , shows three resonances , δ - 4.58 , δ - 13.13 and δ - 19.27 relative intensities 2 : 1 : 1 . The pseudotriplet (δ - 4.58) shows cis couplings to two phosphorus atoms and is assignable as two equivalent axial phosphine ligands , coupled to two inequivalent equatorial phosphine ligands in an octahedral complex.

The two sets of doublets of triplets (δ - 13.13 and δ - 19.27) can then be assigned as the equatorial phosphorus atoms , with the splitting pattern caused by , in each case , cis coupling to the two equivalent axial phosphines and a further cis coupling to the other equatorial phosphine group. It has been tentatively suggested that a σ-aryl group has a greater trans - influence [101] than a σ-alkyl group and the resonances have been assigned accordingly.

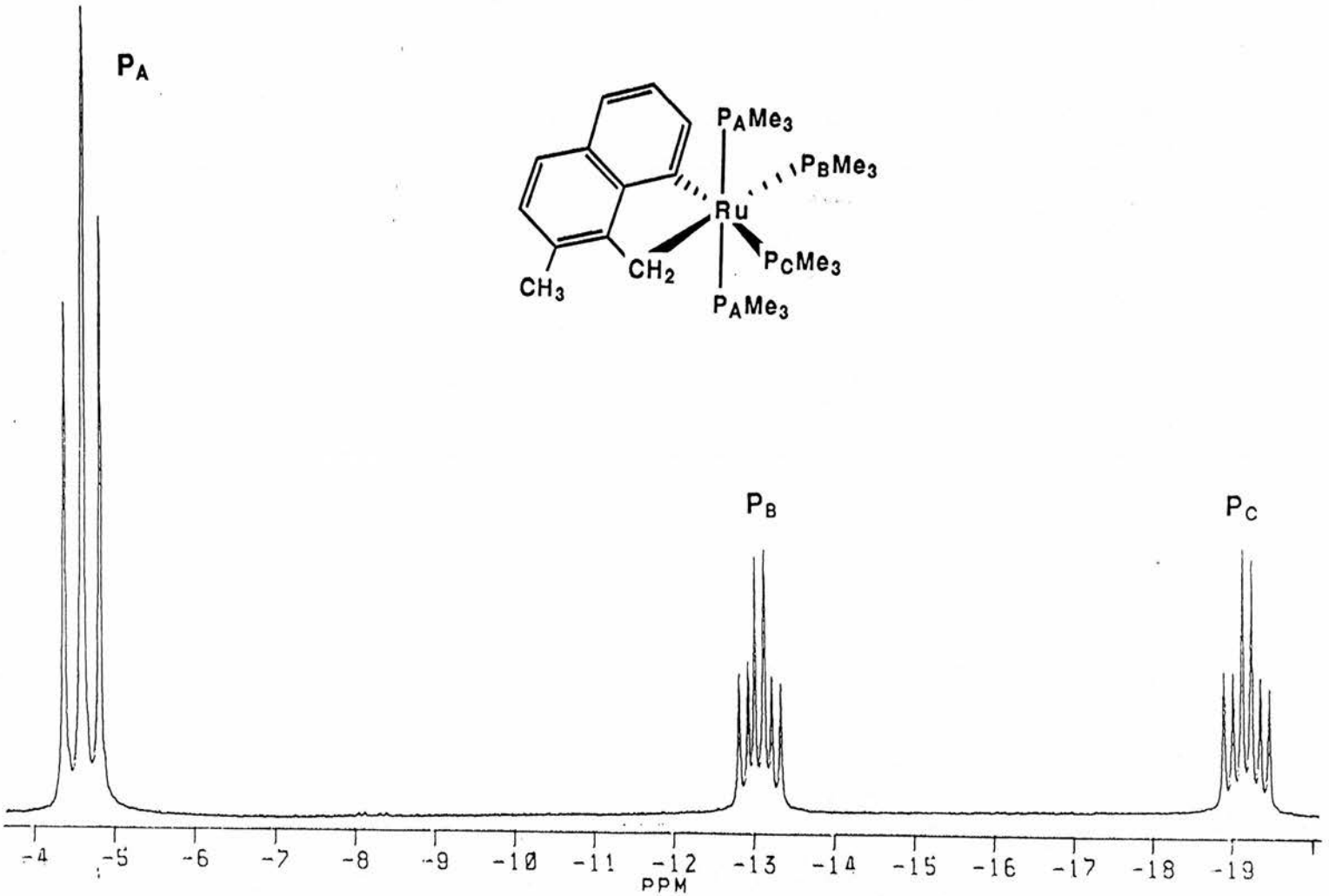


Figure 3.20 The ^{31}P-{^{1}H} n.m.r spectrum of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$ (C_6D_6, 25°C)

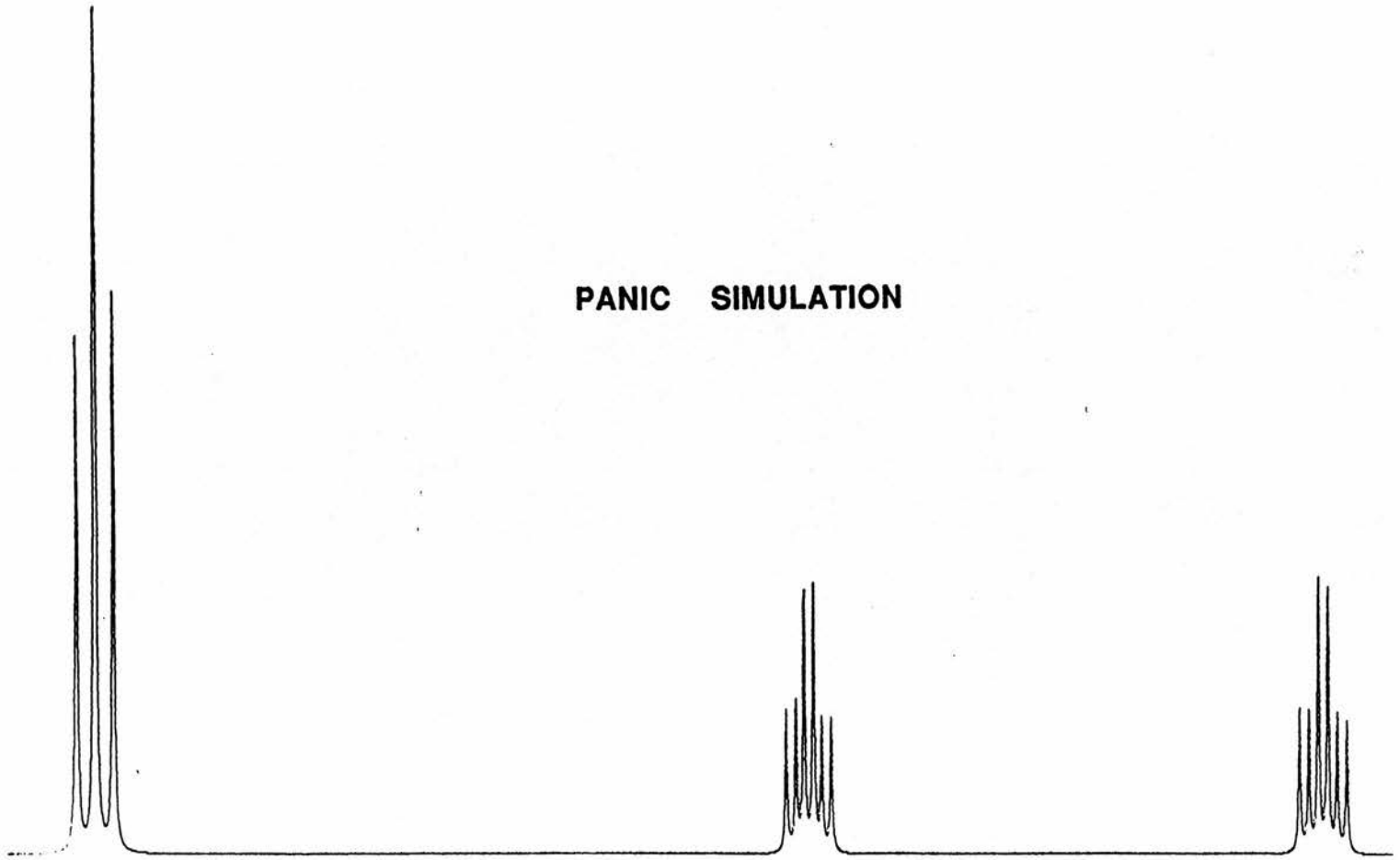


Figure 3.21 The ^{31}P-{^{1}H} n.m.r spectrum of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$ (C_6D_6, 25°C)

^{1}H n.m.r

The ^{1}H n.m.r , (figure 3.22) , contains the expected resonances for the four PMe_3 groups as described from the ^{31}P n.m.r , with doublets for each of the two inequivalent equatorial phosphine groups and an apparent triplet , (figure 3.23) , typical of an $A_nXX'A'_n$ spectrum , with a large value of XX' and consistent with two equivalent axial phosphine groups. Analysis of the aromatic region shows that five aromatic hydrogens are present in the ligand. A singlet resonance at δ 2.84 can be attributed to the CH_3 group on the ligand. The multiplet at δ 2.41 can be assigned as the CH_2 group σ-bonded to ruthenium , and shows the expected couplings to all four phosphine groups.

^{13}C n.m.r

As has been noted previously , very useful diagnostic information can often be obtained from ^{13}C n.m.r spectra , but as yet it has had a tendency to be overlooked by many inorganic chemists.

Once again the spectrum , (figure 3.24) , shows the expected resonances for the four PMe_3 groups , with doublets for each of the two inequivalent equatorial phosphine groups , and an apparent triplet typical of an AXX' spectrum , consistent with two equivalent axial phosphine groups. The resonance observed for the axial phosphine also shows a small triplet splitting due to

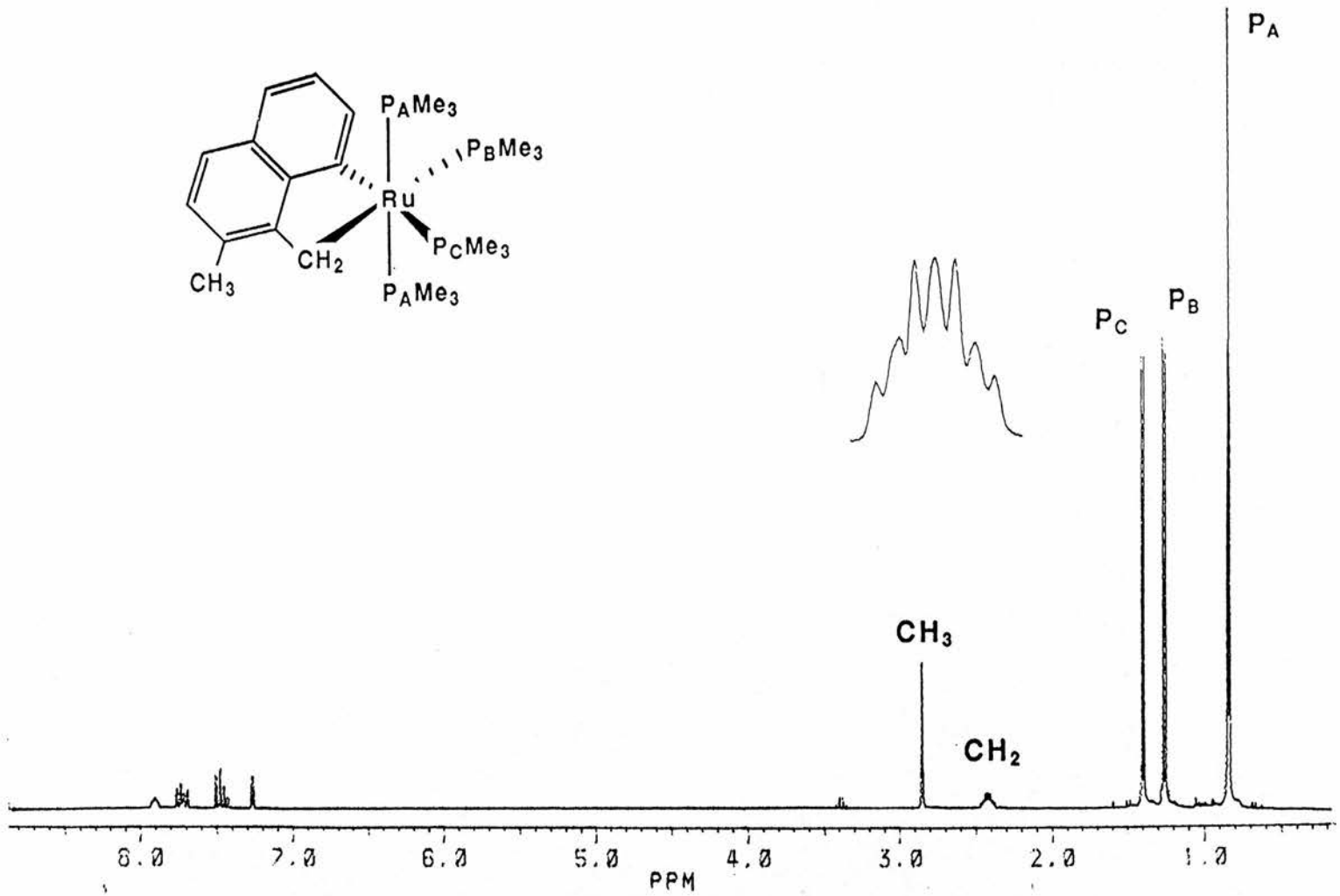


Figure 3.22 The ^1H n.m.r spectrum of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$ (300 MHz) (C_6D_6, 25°C)

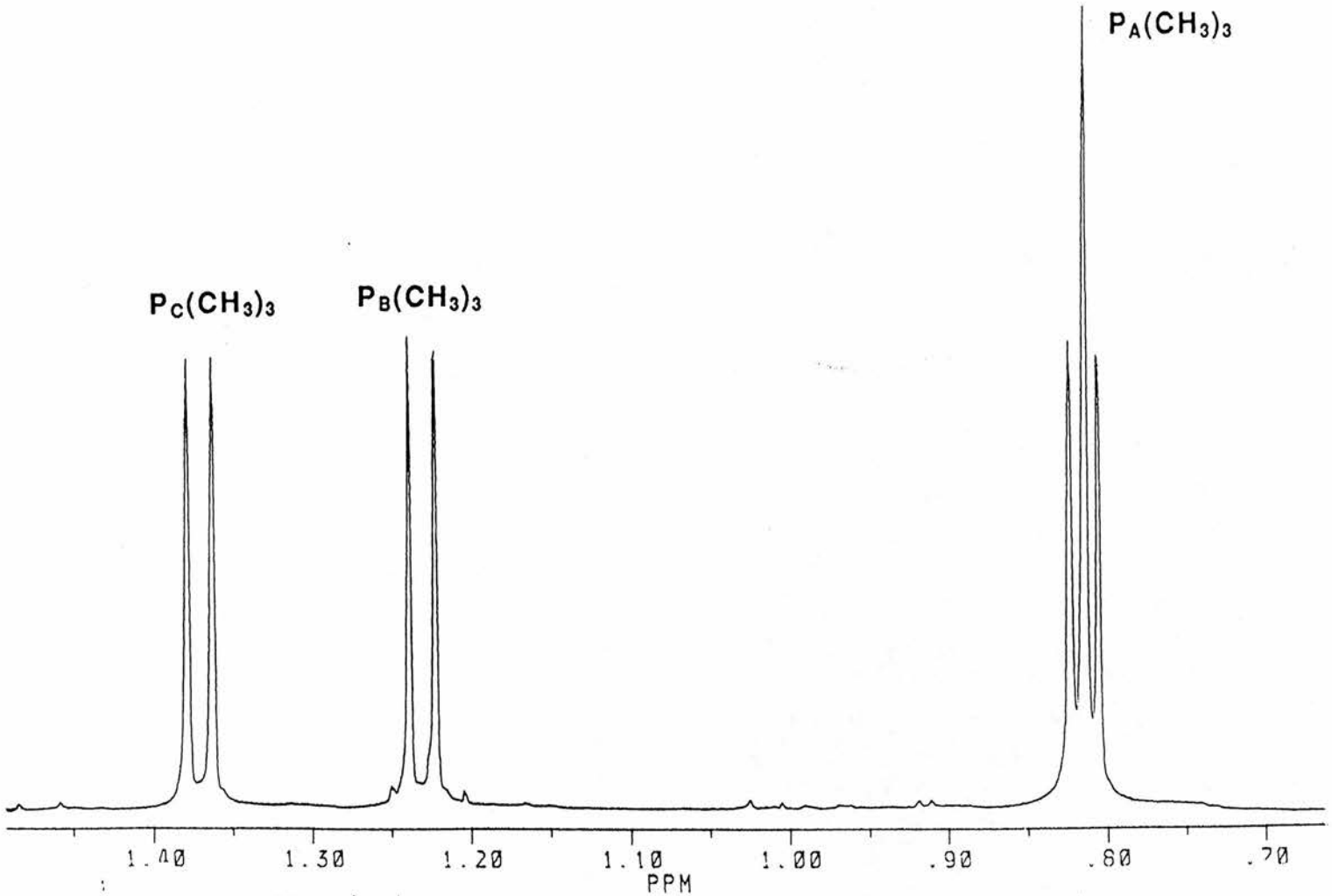


Figure 3.23 The ^1H n.m.r spectrum of the trimethylphosphine resonances of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$ (300 MHz) (C_6D_6, 25°C)

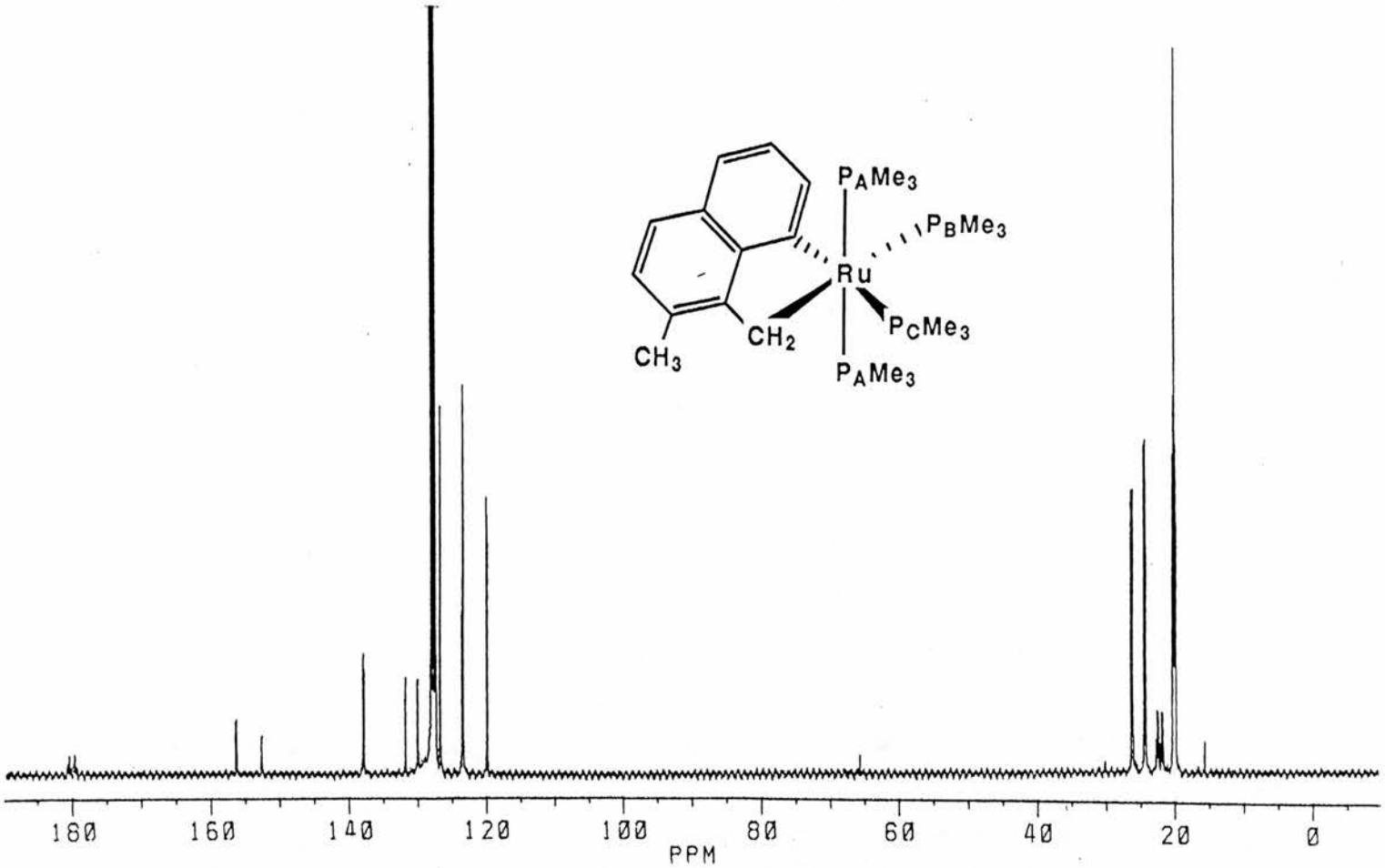
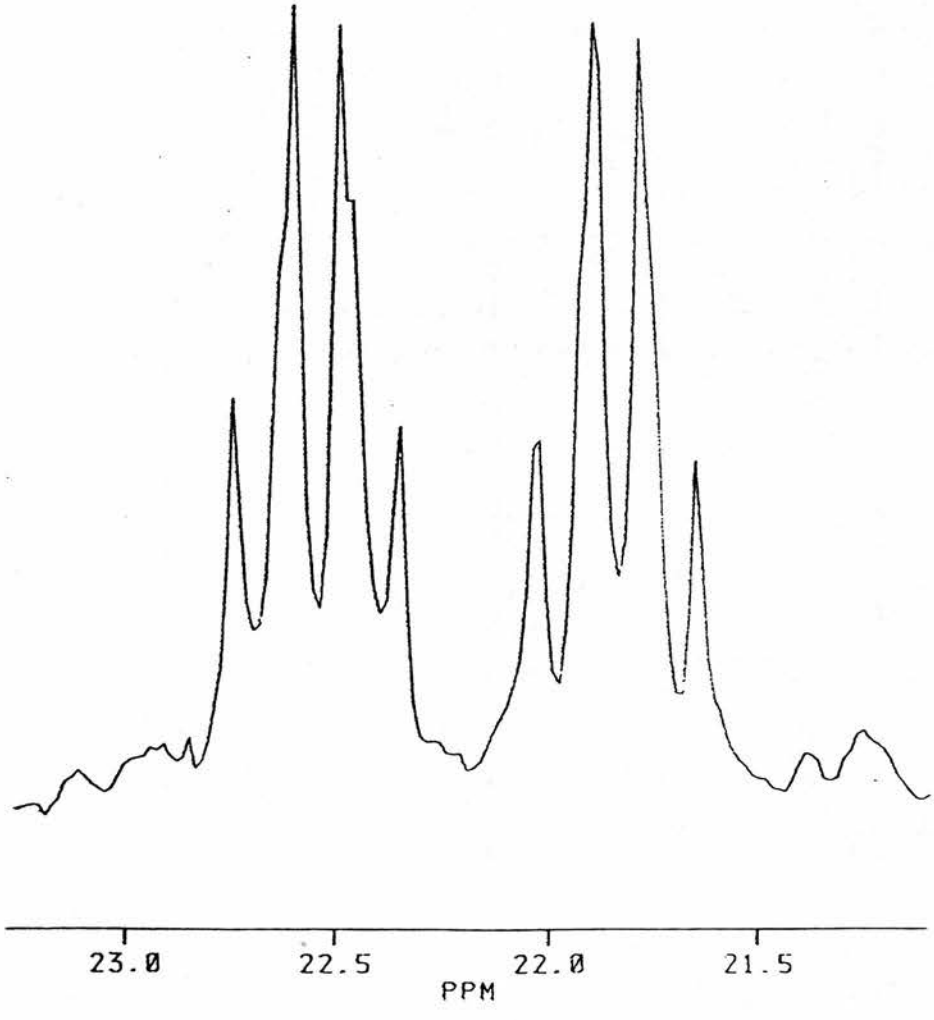
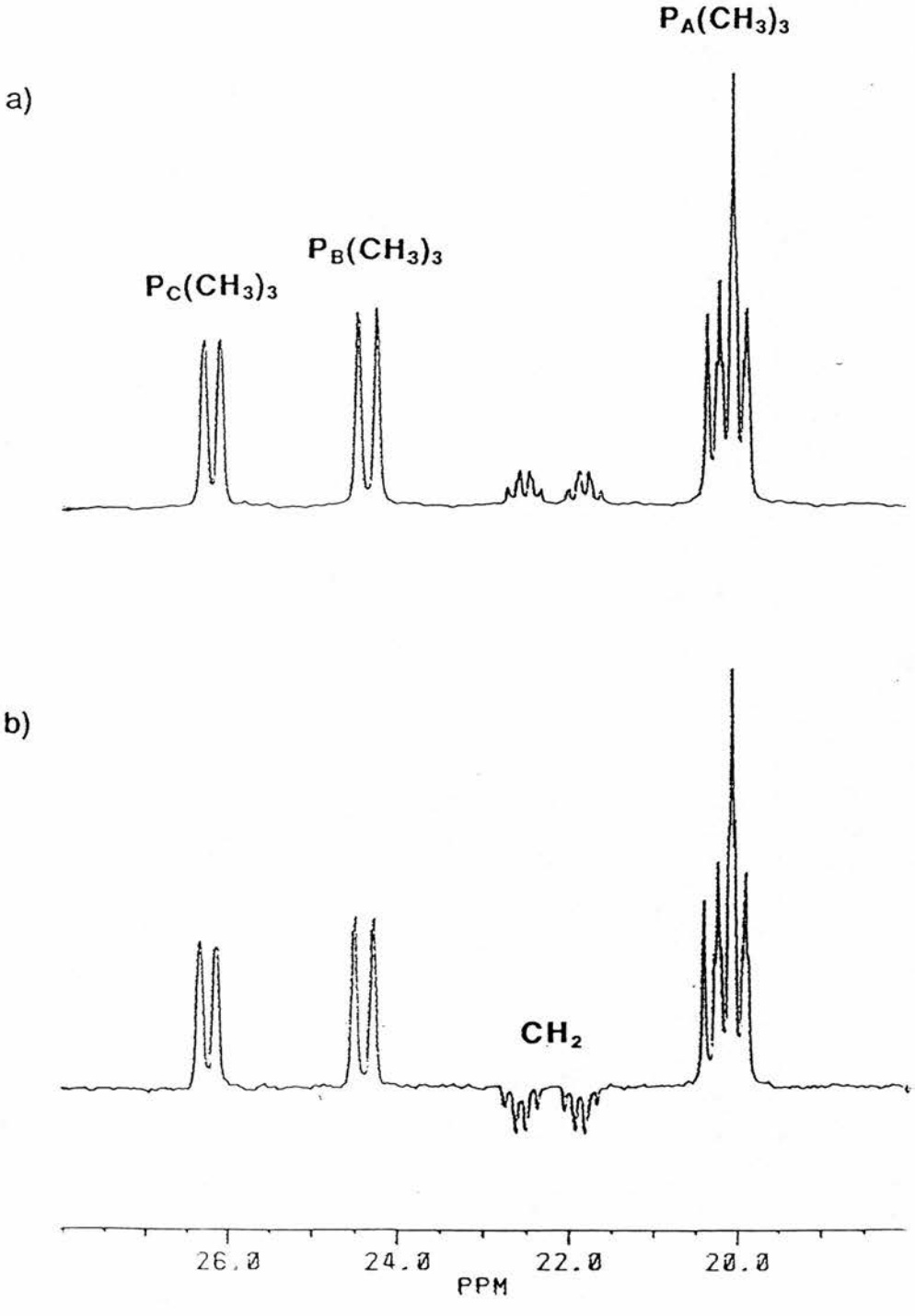


Figure 3.24 The ^{13}C-{^{1}H} n.m.r spectrum of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$ (C_6D_6, 25°C)



The ^{13}C-{^{1}H} n.m.r spectrum of the CH_2 resonance of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$

Figure 3.25



The High Field region of the
^{13}C-{^1H} n.m.r spectrum of $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$

a) Normal pulse sequence
b) DEPT-135 pulse sequence

Figure 3.26

further coupling of the phosphine carbons to the two equatorial phosphorus atoms. A singlet resonance (δ 20.51) is observed for the CH_3 group. A pseudo doublet of quartets (δ 22.19) , (figure 3.25) , is suggested as the methylene carbon resonance. This is confirmed by a DEPT-135 pulse sequence (figure 3.26). The splitting pattern can be attributed to the expected trans phosphorus coupling and three cis phosphorus couplings.

This result suggests that in fact lithiation of 1,2-dimethylnaphthalene occurs at both the 1- and 2- positions and not specifically the 2- position as speculated upon earlier.

Lithiation at the 2-position will lead only to the 1,2-naphthoquinodimethane whereas metallation at the 1- position can lead via δ-hydrogen abstraction to either the 1,2-naphthoquinodimethane or $[Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4]$. This result also explains why a similar product was not observed in the 2,3-dimethylnaphthalene case.

The product obtained from the reaction of $[RuCl_2(PMe_2Ph)_4]$ and 2-lithiomethyl-3-methylnaphthalene.TMEDA , as already stated , is not the expected naphthoquinodimethane complex. The complex has not been obtained in an analytically pure form , but resonances in the δ 3 - 6 region of the ^1H n.m.r spectrum are similar to those of the η^3-bound o-methylbenzyl ligand in

[$Rh(o\text{-}CH_2C_6H_4CH_3)(PPh_3)_2$]. The ^{31}P n.m.r spectrum shows that there are three phosphine ligands in mutually cis positions. On this basis the compound has been tentatively assigned as [$RuX(o\text{-}CH_2C_{10}H_6CH_3)(PMe_2Ph)_3$] , with X being either chloride or a σ-bonded $o\text{-}CH_2C_{10}H_6CH_3$ ligand (it is not hydride).

3.7 Mechanistics

The exact mechanism by which these complexes form is still unclear.

Attempts at the interconversion of [$Ru(1,2\text{-}CH_2C_{10}H_6CH_2)(PMe_3)_3$] and [$Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4$] have been made by refluxing the former with excess PMe_3 , or by treating the latter with S_8 , (a well known phosphine scavenger) , photolysis or by extensive reflux in the absence of added phosphine. In none of these cases is the interconversion achieved and therefore as expected , neither is on the reaction pathway to the other. It seems therefore that loss of phosphine is important in the determination of the nature of the products.

For $P = PMe_3$, loss of phosphine must presumably occur after alkylation of at least one Ru - Cl bond (probably after both - section 2.12) , since it has been shown previously that loss of phosphine from [$RuCl_2(PMe_3)_4$] would allow alkylation by Grignard reagents , but that this reaction is not observed.

For P = PMe_2Ph or PPh_2Me the phosphines are very much more labile , phosphine loss from the dihalides is known to be facile and alkylation by Grignards is observed.

The schemes , (figures 3.27 , 3.28 and 3.29) , offer partial explanations for the formation of the various different products observed which are supported by the following observations.

[$RuCl_2(PMe_3)_4$] has trans stereochemistry and attempts to isomerize it to cis even under very forcing conditions have not been successful. It is probable therefore that alkylation occurs trans to Cl. The high trans influence of the alkyl ligand will then labilize the remaining chloride.

Removal of a hydrogen from a methyl group α to a coordinated allyl moiety has been shown to be facile in low valent ruthenium phosphine complexes [122].

In the case of the reaction involving [$RuCl_2(PMe_2Ph)_4$] and 2-lithiomethyl-3-methylnaphthalene.TMEDA it may be that a marked preference for forming the allyl complex with the unsubstituted ring carbon atom precludes the further deprotonation of the other methyl group.

It appears then that not only is the lability of the phosphine important in the mechanism but also the stability of the

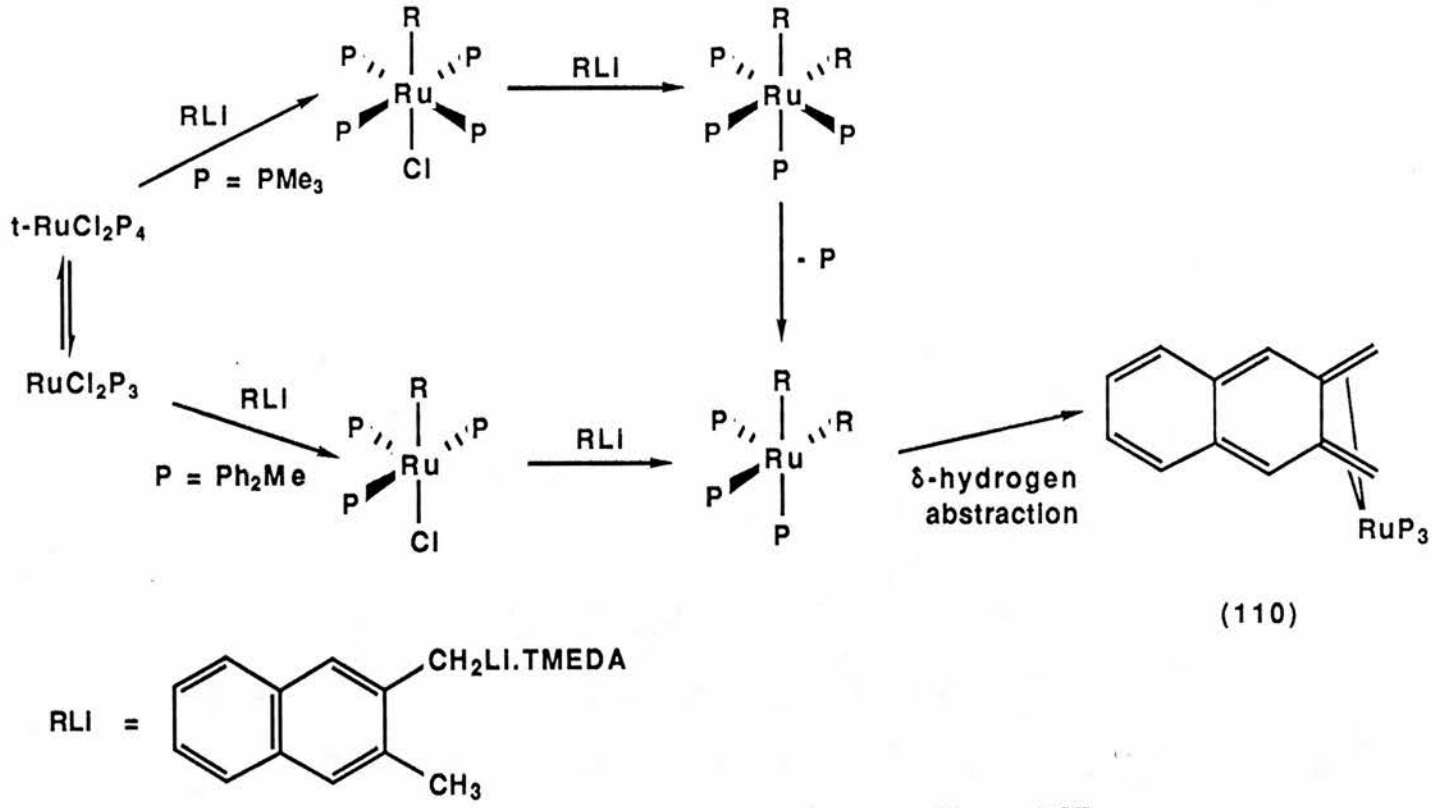

RLI
P = PMe3
t-RuCl2P4
RuCl2P3
RLI
P = Ph2Me
RLI
RLI
- P
δ-hydrogen
abstraction
RuP3
(110)
RLI =
CH2LI.TMEDA
CH3

Figure 3.27

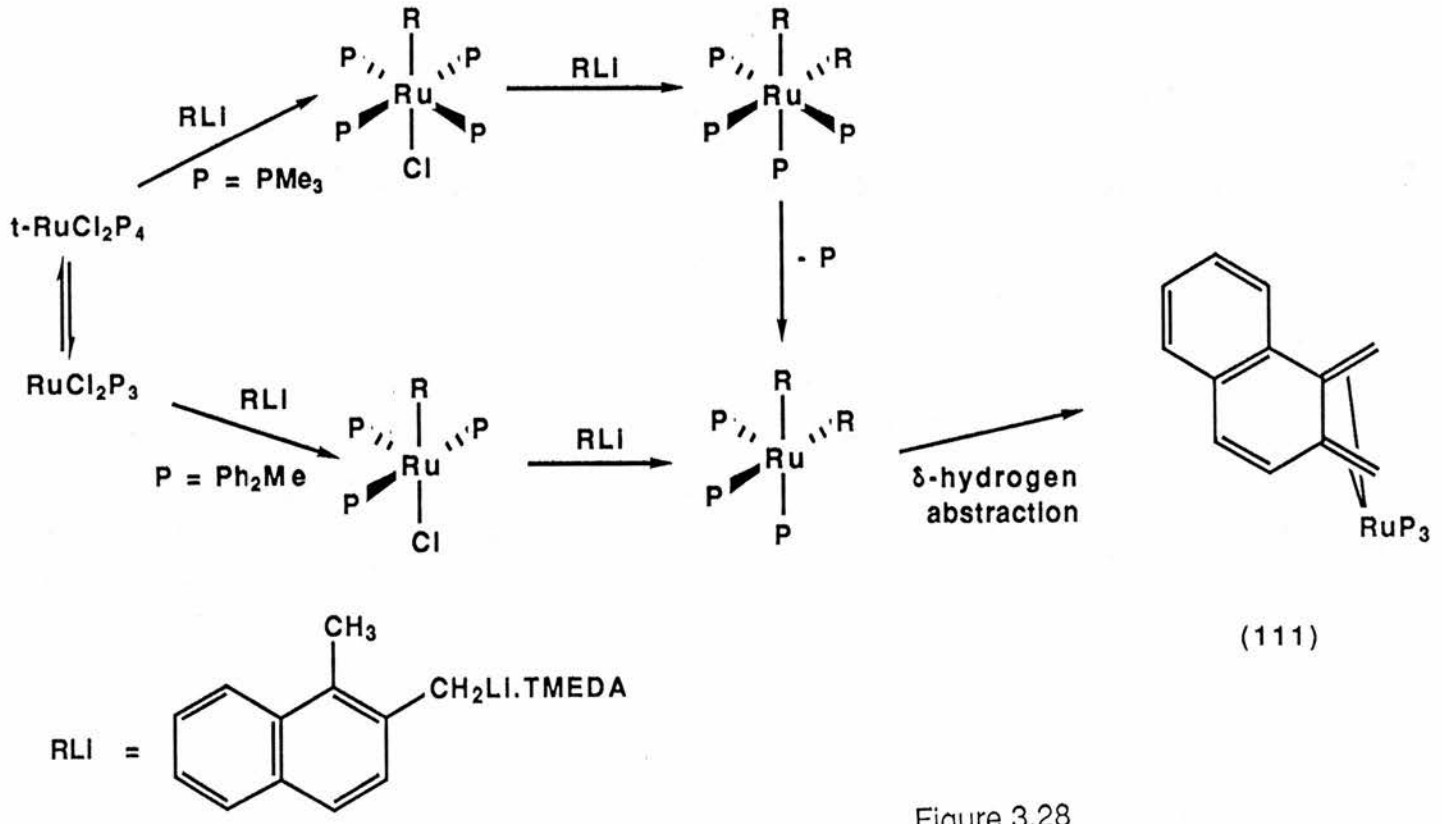

RLI
P = PMe3
t-RuCl2P4
RuCl2P3
RLI
P = Ph2Me
RLI
RLI
- P
δ-hydrogen
abstraction
RuP3
(111)
RLI =
CH3
CH2LI.TMEDA

Figure 3.28

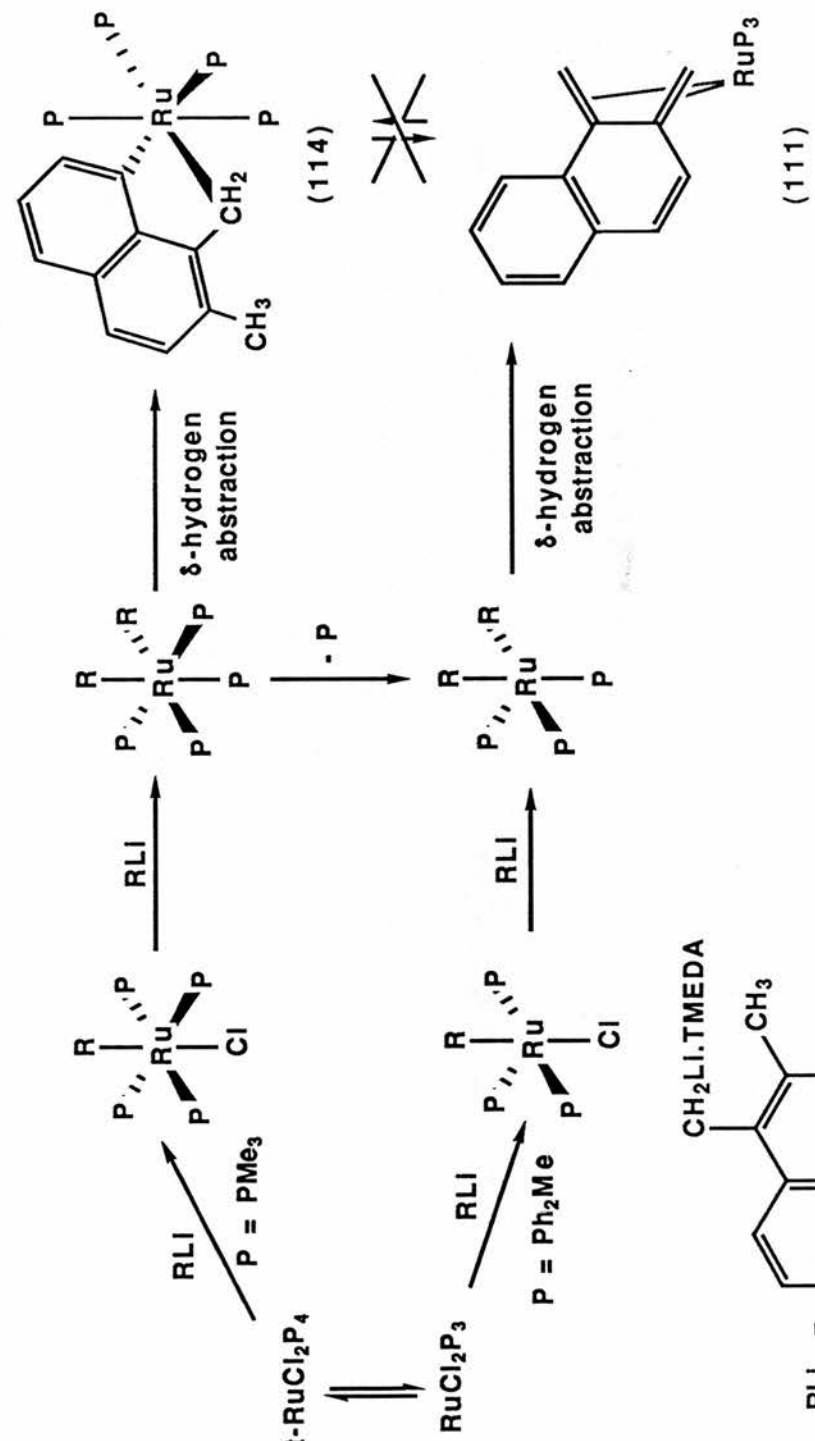

t-RuCl2P4
RuCl2P3
P = PMe3
P = Ph2Me
RLI
RLI
RLI
RLI
- P
δ-hydrogen abstraction
δ-hydrogen abstraction
(114)
(111)
RuP3
CH2LI.TMEDA
RLI =

Figure 3.29

complexes that can be formed.

If RLi = 2-lithiomethyl-3-methylnaphthalene.TMEDA or 2-lithiomethyl-1-methylnaphthalene.TMEDA only one stable product can be formed , the naphthoquinodimethane , via either a δ (C-H-Ru) two-electron agostic interaction or a δ (C-H) oxidative addition involving the o-methyl group.

If RLi = 1-lithiomethyl-2-methylnaphthalene.TMEDA then the lability of the phosphine becomes particularly important. If P = PPh_2Me or PMe_2Ph then loss of phosphine is rapid and once again the only product that is formed is the naphthoquinodimethane. If P = PMe_3 then phosphine loss is not rapid and there is now the added possibility of a similar δ (C-H-Ru) agostic interaction with the hydrogen on the 8-position of the naphthalene ring , before a phosphine is lost , and leading to [$Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4$].

3.8 Synthesis

The synthesis of the o-naphthoquinodimethane complexes of ruthenium was based on the method developed for the preparation of the o-quinodimethane complexes and contained the same inherent problems , compounded somewhat by the much higher

boiling points of the organic precursors , 2,3-dimethylnaphthalene , (269°C) , and 1,2-dimethylnaphthalene , (268°C). The reactions also showed much higher proportions of impurities. The resulting difficulties in purification , (column chromatography was again no use) , meant that a number of the compounds , although characterized by spectroscopic means , have no accurate microanalytical data.

Many of the impurities present in the formation of these o-naphthoquinodimethane complexes have been detected in the reactions involving syntheses of the o-quinodimethane complexes , however the relative amounts in those cases were comparatively small and did not affect crystallization in the same way. It is interesting that whilst the use of [$RuCl_2(PMe_2Ph)_4$] and [$RuCl_2(PPh_2Me)_4$] resulted , here , in significant amounts of impurities , (particularly with [$RuCl_2(PPh_2Me)_4$]) , the use of [t-$RuCl_2(PMe_3)_4$] resulted in a very much cleaner reaction mixture.

As has been indicated a number of times now , phosphine loss from the dihalides [$RuCl_2(PPh_2Me)_4$] and [$RuCl_2(PMe_2Ph)_4$] is known to be facile , (PPh_2Me is more labile than PMe_2Ph) , but is not observed for [t-$RuCl_2(PMe_3)_4$]. It would therefore tend to suggest that this is an important factor in the formation of the impurities. The very fact however that there is a difference between the syntheses of o-quinodimethane and

o-naphthoquinodimethane complexes suggests that the lithium reagents must also have a significant part to play.

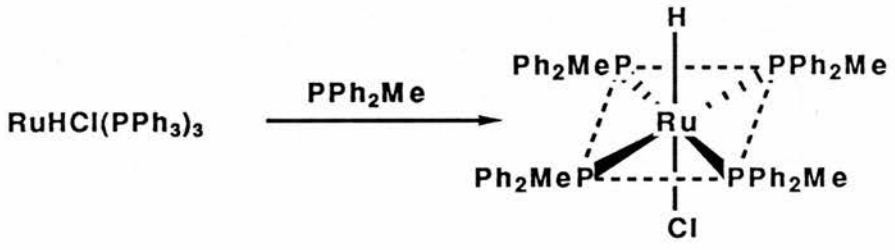
The reactions involving [$RuCl_2(PPh_2Me)_4$] produce two main impurities which have not been isolated. The first has a ^{31}P n.m.r spectrum which shows two triplets , (δ 33.6 , $^2J_{PP}$ = 18.4 Hz , P_A ; δ 23.47 , $^2J_{PP}$ = 18.4 Hz , P_B) , and is assignable as a cis - configuration of four phosphine groups. This can be identified as cis - dihydrotetrakis(methyldiphenylphosphine)ruthenium(II) [123] , [cis-$H_2Ru(PPh_2Me)_4$] . The assignment of the P_A and P_B phosphorus atoms can be made by a consideration of the trans effect. Both P_A atoms are trans to phosphorus and would be expected at higher frequency than the P_B phosphorus atoms which are trans to hydrogen [101].

The second impurity appears as a singlet , (δ 23.9) , in the ^{31}P n.m.r spectrum , and was thought to be trans - chlorohydrido - tetrakis(methyldiphenylphosphine)ruthenium(II) , [t-$RuHCl(PPh_2Me)_4$] .

3.8.1 Preparation of [t-$RuHCl(PPh_2Me)_4$]

The synthesis relies on the common technique of ligand - exchange. Thus when [$RuHCl(PPh_3)_3$] is stirred with a 6 molar equivalent of PPh_2Me in light petroleum ether for 12 hours , a

yellow solid is obtained which can be easily recrystallized from diethyl ether , (figure 3.30).



(116)

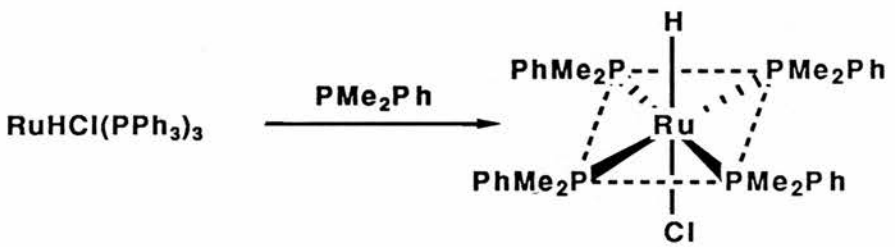
Figure 3.30

A quintet splitting pattern in the hydride region of the ^{1}H n.m.r (δ -17.80 , $^{2}J_{PH} = 20.84$ Hz) and a singlet in the ^{31}P n.m.r (δ 20.09) confirm the assignment as the expected product [t-$RuHCl(PPh_2Me)_4$] , (**116**) .

3.8.2 Preparation of [t-$RuHCl(PMe_2Ph)_4$]

[$RuHCl(PPh_3)_3$] was stirred with a 6 molar equivalent of PMe_2Ph in light petroleum ether for 18 hours a yellow solution was obtained , (figure 3.31) , from which the product could not be easily separated due to its solubility , but which could be identified by n.m.r. Again there is a quintet spitting pattern in the hydride region of the ^{1}H n.m.r (δ -18.28 , $^{2}J_{PH} = 20.47$ Hz) and a

singlet in the ^{31}P n.m.r (δ 8.94) confirming the assignment as the expected product , [t-$RuHCl(PMe_2Ph)_4$] , (**117**).



(117)

Figure 3.31

The ^{31}P n.m.r would seem to suggest that the second impurity obtained from the reaction of [$RuCl_2(PPh_2Me)_4$] with lithium reagents derived from dimethylnaphthalenes is not [t-$RuHCl(PPh_2Me)_4$]. The impurities in the reaction mixtures using [t-$RuCl_2(PMe_2Ph)_4$] cannot be ascribed to either the [cis - $H_2Ru(PMe_2Ph)_4$] or the [t-$RuHCl(PMe_2Ph)_4$]. Despite these findings and the less than in depth study on the identity of the impurities it would still seem that the lability of the phosphines and the preparation of the lithium reagents are the important factors in the formation of impurities.

The normal method of lithium reagent preparation is based upon a transmetallation reaction between a 1 : 1 mixture of BuLi.TMEDA and the organic substrate , whether it be a

polymethylbenzene or a dimethylnaphthalene. Reaction of the lithium salt of 2,3-dimethylnaphthalene , prepared in this manner , with methyl iodide and analysis of the products by GC - MS showed that the major product was 2-ethyl-3-methylnaphthalene , and that therefore the major product of the transmetallation reaction is as suggested by Dunkelblum and Hart [117] the mono-metallated naphthalene , 2-lithiomethyl-3-methylnaphthalene. TMEDA. The GC - MS also shows however that approximately 30% of the starting material (2,3-dimethylnaphthalene) is unreacted. If 30% of the 2,3-dimethylnaphthalene is unreacted then it can be assumed that 30% of the BuLi.TMEDA is also unreacted , since no other products were obtained.

The impurities observed when preparing the o-quinodimethane and o-naphthoquinodimethane complexes may possibly be accounted for by a competition process between the polymethylbenzene , dimethylnapthalene lithium reagents and residual BuLi.TMEDA. The lability of the phosphine groups in [$RuCl_2(PPh_2Me)_4$] and [$RuCl_2(PMe_2Ph)_4$] presumably enhances this competition process and attack of BuLi.TMEDA is much faster than attack of the sterically more demanding polymethylbenzene , and dimethylnaphthalene lithium reagents. Lack of a labile phosphine group in [t-$RuCl_2(PMe_3)_4$] hinders this competition process , rates of attack of the lithium reagents are now comparable and the large excess of the polymethylbenzene , dimethylnaphthalene lithium reagents over the

residual BuLi.TMEDA results in very small amounts of impurities.

On this basis the absence of any substantial quantities of impurities in the o-quinodimethane reactions suggests that the preparation of the lithium reagents of the polymethylbenzene precursors proceed almost to completion and that therefore very little BuLi.TMEDA remains unreacted. It might also be noted that excesses of organic substrate can and were used in many of the preparations of lithium reagents of the polymethylbenzenes, to prevent residual BuLi.TMEDA, since in most cases the excess could later be easily removed. This was not the case for the dimethylnaphthalenes where even minor quantities of dimethylnaphthalene caused severe problems with purification.

This idea that it is the residual BuLi.TMEDA creating the contaminants is further borne out by results of the early preparations of the o-naphthoquinodimethane complexes. Before a titration procedure was introduced for determining the concentration of a particular lithium solution, large excesses (~ 10 fold) of the lithium reagents were used and resulted in considerably larger proportions of impurities. The larger excesses of lithium reagents would have resulted in larger amounts of BuLi.TMEDA which if as has been suggested reacts at a greater rate than the naphthalene lithium reagent would have produced higher proportions of contaminants.

Final confirmation of the role of residual BuLi.TMEDA in producing the impurities is provided when BuLi.TMEDA in

diethyl ether is reacted with [$RuCl_2(PPh_2Me)_4$]. The ^{31}P n.m.r shows absorptions which exactly correspond to those present in reaction solutions of the dimethylnaphthalene lithium reagents and [$RuCl_2(PPh_2Me)_4$].

The preparation of the dimethylnaphthalene lithium reagents as described, results in most cases, in an oil from which the supernatant petroleum ether can be removed by filtration. Clearly while this must remove some unreacted BuLi.TMEDA it is not entirely successful. It would be ideal to prepare a lithium reagent which is a crystalline solid and which can be washed with diethyl ether. Use of the base pentamethyldiethylenetriamine provides such crystalline salts [124] and there is the added advantage that precise quantities of reagent can be weighed out rather than using a crude titration technique. This may then be the future of the preparations of o-quinodimethane and o-naphthoquinodimethane complexes of ruthenium.

3.9 Experimental

Tris(methyldiphenylphosphine)(2-α,3-α':η⁴-o-naphthoquinodimethane)ruthenium(0)

The complex [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028×10^{-3} mol) was stirred with a solution of

2-lithiomethyl-3-methylnaphthalene.TMEDA (2.5 x 10^{-3} mol) in diethyl ether (40 cm^3). After 24 h , water (20 cm^3) was added to the red solution and after stirring for 30 min., the ether was decanted , dried over anhydrous magnesium sulphate , and the ether removed in vacuo. Excess 2,3-dimethylnaphthalene and free $PMePh_2$ were removed by sublimation at 140°C onto a cold finger (- 78°C). The resulting red gum was dissolved into diethyl ether. After filtration , concentration , and cooling to - 30°C for several days , the product separated as red crystals , which were collected and dried in vacuo. Yield 0.35 g (40 %). ^1H n.m.r (benzene-d_6 ,80 MHz , 298 K) : δ 7.61 - 6.13 (complex ,aromatic) ; δ 2.16 (d , $^2J_{PH}$ = 7.8 Hz , P_AMe) ; δ 1.74 (pdd , $^2J_{HH}$ = 4.5 Hz , $^3J_{PH}$ = 5.5 Hz , H_B) ; δ 1.50 (pd , $^2J_{PH}$ + $^4J_{PH}$ = 4.1 Hz , P_BMe) ; δ 0.73 (pdd , $^2J_{HH}$ = 4.5 Hz , $^3J_{PH}$ = 4.5 Hz , H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 41.4 (t , $^2J_{PP}$ = 4.0 Hz , P_A) ; δ 19.5 (d , $^2J_{PP}$ = 4.0 Hz , P_B). Found : C , 70.7 ; H , 7.0. $C_{51}H_{49}P_3Ru$ requires : C , 71.6 ; H , 5.8.

The following complexes were similarly prepared , but with the work-up after the sublimation step as described.

Tris(trimethylphosphine)(2-α,3-α':η⁴-o-naphthoquinodimethane)ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55 g , 1.155 x 10^{-3} mol) and 2-lithiomethyl-3-methylnaphthalene.TMEDA (3.0 x 10^{-3} mol) in diethyl ether (40 cm^3). The red-brown solid was washed with light petroleum ether and dried in vacuo. Yield 0.22 g (40 %). ^1H n.m.r (benzene-d_6 , 80 MHz , 298 K) : δ 7.95 - 7.10 (complex , aromatic) ; δ 2.26 (pdd , $^2J_{HH}$ = 4.5 Hz , $^3J_{PH}$ = 8.0 Hz , H_B) ; δ 1.42 (d , $^2J_{PH}$ = 8.1 Hz , P_AMe) ; δ 0.94 (pd , $^2J_{PH} + {}^4J_{PH}$ = 5.8 Hz ,P_BMe) ; δ 0.49 (pdd , $^2J_{HH}$ = 4.5 Hz , $^3J_{PH}$ = 6.2 Hz , H_A). ^{31}P-{^1H} n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 28.5 (t , $^2J_{PP}$ = 10.7 Hz , P_A) ; δ 0.16 (d , $^2J_{PP}$ = 10.7 Hz , P_B). Found : C , 51.8 ; H , 7.5 . $C_{21}H_{37}P_3Ru$ requires : C , 52.5 ; H , 7.7 .

Reaction as above of [$RuCl_2(PMe_2Ph)_4$] ,(0.75 g , 1.035 x 10^{-3} mol) , with 2-lithiomethyl-3-methylnaphthalene.TMEDA (2.5 x 10^{-3} mol).

The red - orange gum was extracted into hot petroleum ether. After concentration a brown solid formed. It could not be further purified but was tentatively assigned as [$RuCl(\eta^3\text{-}CH_2C_{10}H_6Me)(PMe_2Ph)_3$] from its spectroscopic

properties.

^1H n.m.r (benzene-d_6 , 80 MHz , 298 K): δ 8.0 - 6.5 (complex , aromatic) ; δ 6.25 (bt , J = 7.0 Hz) ; δ 5.45 (d , J = 7.7 Hz) ; δ 4.0 (q , J = 9.0 Hz) ; δ 2.42 (dd , J = 6.0 Hz , 6.5 Hz) ; δ 2.2 - 0.6 (complex). ^{31}P-{^1H} n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 11.5 (d , $^2J_{PP}$ = 12.3 Hz) ; δ 10.8 (d , $^2J_{PP}$ = 13.2 Hz) ; δ 6.1 (t , $^2J_{PP}$ = 12.3 Hz , $^2J_{PP}$ = 13.2 Hz).

Tris(methyldiphenylphosphine)(1-α,2-α':η^4-o-naphthoquinodimethane)ruthenium(0)

From [$RuCl_2(PPh_2Me)_4$] (1.0 g , 1.028 x 10^{-3} mol) and the lithium salt of 1,2-dimethylnaphthalene , (2.5 x 10^{-3} mol) in diethyl ether (40 cm^3). The orange gum was dissolved in diethyl ether (1 cm^3) and syphoned into light petroleum ether (40 cm^3) pre-cooled to -78°C. The resulting yellow solid which was collected and dried in vacuo was contaminated with [$H_2Ru(PPh_2Me)_4$] (up to 10 %) which could not be removed. Yield 0.35 g. ^1H n.m.r (benzene-d_6 , 80 MHz , 298 K) : δ 8.00 - 6.10 (complex aromatic) ; δ 2.55 (bm , H_B) ; δ 2.28 (d , $^2J_{PH}$ = 6.8 Hz , P_AMe) ; δ 2.04 (bm , $H_{B'}$) ; δ 1.55 (d , $^2J_{PH}$ = 5.8 Hz ,

P_BMe) ; δ 1.35 (d , $^2J_{PH}$ = 5.7 Hz , P_CMe) ; δ 0.38 (bm , [2H] , $H_{A'}$, H_A). ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 30.2 (s , P_A) ; δ 20.3 (d , $^2J_{PP}$ = 24.2 Hz , P_B) ; δ 15.6 (d , $^2J_{PP}$ = 24.2 Hz , P_C).

Tris(dimethylphenylphosphine)(1-α,2-α':η^4-o-naphthoquinodimethane)ruthenium(0)

From [$RuCl_2(PMe_2Ph)_4$] (0.75 g , 1.035 x 10^{-3} mol) and the lithium salt of 1,2-dimethylnaphthalene (3.0 x 10^{-3} mol) in diethyl ether (40 cm^3). The orange gum was dissolved in diethyl ether (2 cm^3) and syphoned into light petroleum ether (40 cm^3) pre-cooled to -78°C. The yellow-orange solid was collected and dried in vacuo. The ^{31}P n.m.r showed traces of unidentified impurities. Yield 0.26 g (38 %). ^{1}H n.m.r (benzene-d_6 , 80 MHz , 298 K) : δ 8.20 - 6.10 (complex , aromatic) ; δ 2.53 (bm , H_B) ; δ 2.16 (bm , $H_{B'}$) ; δ 1.75 (d , $^2J_{PH}$ = 7.7 Hz , [6H] , P_A) ; δ 1.15 (d , $^2J_{PH}$ = 5.8 Hz , PMe) ; δ 1.03 (d , $^2J_{PH}$ = 6.0 Hz , PMe) ; δ 0.99 (d , $^2J_{PH}$ = 5.7 Hz , PMe) ; δ 0.95 (d , $^2J_{PH}$ = 6.0 Hz , PMe) ; δ - 0.45 (bm , [2H] , $H_{A'}$, H_A) . ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 20.1 (pt , $^2J_{PP}$ = 3.5 Hz , $^2J_{PP}$ = 3.9 Hz , P_A) ; δ

4.1 (dd , $^2J_{PP}$ = 3.5 Hz , $^2J_{PP}$ = 29.6 Hz , P_B) ; δ 2.7 (dd , $^2J_{PP}$ = 3.9 Hz , $^2J_{PP}$ = 29.6 Hz , P_C).

Tris(trimethyphosphine)(1-α,2-α':η^4-o-naphthoquinodimethane)ruthenium(0)

From [$RuCl_2(PMe_3)_4$] (0.55 g , 1.155 x 10^{-3} mol) and the lithium salt of 1,2-dimethylnaphthalene (3.0 x 10^{-3} mol) in diethyl ether (40 cm^3). The yellow gum was extracted with light petroleum ether to leave a yellow powder which was recrystallized from toluene and light petroleum , and was identified as tetrakis(trimethylphosphine)(7-methyl-8-methylene -1-naphthyl)ruthenium(II) , [$Ru(C_{10}H_5\{CH_3\}CH_2)(PMe_3)_4$]. Yield 0.07 g (11 %) . ^1H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 7.96 - 7.41 (complex , 5H) ; δ 2.84 (s , CH_3) ; δ 2.41 (m , $^3J_{PH}$ = 4.67 Hz , $^3J_{PH}$ = 4.67 Hz , $^3J_{PH}$ = 8.27 Hz , $^3J_{PH}$ = 8.82 Hz , CH_2) ; δ 1.37 (d , $^2J_{PH}$ = 4.64 Hz , $P_C(CH_3)_3$) ; δ 1.23 (d , $^2J_{PH}$ = 5.37 Hz , $P_B(CH_3)_3$) ; δ 0.81 (at , $^2J_{PH} + {}^4J_{PH}$ = 5.13 Hz , $P_A(CH_3)_3$) . ^{13}C-{^1H} n.m.r (benzene-d_6 ,75.47 MHz , 298 K) : δ 26.25 (d , $^1J_{PC}$ =14.08 Hz ,$P_C(CH_3)_3$) ; δ 24.40 (d ,$^1J_{PC}$ = 15.26 Hz , $P_B(CH_3)_3$) ; δ 22.19 (pdq , $^2J_{PC}$ = 9.24 Hz , $^2J_{PC}$ = 9.23 Hz , $^2J_{PC}$ = 9.23 Hz ,

$^2J_{PC}$ = 52.98 Hz , CH_2) ; δ 20.51 (s , CH_3) ; δ 20.13 (at , $^1J_{PC} + {}^3J_{PC}$ = 36.38 Hz , $P_A(CH_3)_3$). $^{31}P-\{^1H\}$ n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ - 4.59 (at , $^2J_{PP}$ = 27.51 Hz , $^2J_{PP}$ = 25.70 Hz , $^2J_{PP}$ = 27.43 Hz , $^2J_{PP}$ = 25.20 Hz , P_A) ; δ - 13.13 (dt , $^2J_{PP}$ = 13.78 Hz , $^2J_{PP}$ = 25.70 Hz , $^2J_{PP}$ = 25.20 Hz , P_B) ; δ - 19.27 (dt , $^2J_{PP}$ = 13.78 Hz , $^2J_{PP}$ = 27.51 Hz , $^2J_{PP}$ = 27.43 Hz , P_C). Found : C , 51.8 ; H , 8.2. $C_{24}H_{46}P_3Ru$ requires : C , 51.5 ; H , 8.3.

The petroleum ether solution was concentrated and on cooling to -30°C gave yellow crystals which were collected and dried in vacuo. These were identified as [$Ru(CH_2C_{10}H_6CH_2)(PMe_3)_3$]. Yield 0.13 g (24 %). ^1H n.m.r (benzene-d_6 , 300 MHz , 298 K) : δ 8.42 - 7.04 (complex , aromatic) ; δ 2.65 (bm , H_B) ; δ 1.98 (bm , $H_{B'}$) ; δ 1.46 (d , $^2J_{PH}$ = 8.1 Hz , P_AMe) ; δ 1.00 (d , $^2J_{PH}$ = 6.1 Hz , P_BMe) ; δ 0.64 (d , $^2J_{PH}$ = 6.0 Hz , P_CMe) ; δ - 0.07 (bm , $H_{A'}$) ; δ - 0.32 (bm , H_A). $^{31}P-\{^1H\}$ n.m.r (benzene-d_6 , 32.20 MHz , 298 K) : δ 8.0 (pt , $^2J_{PP}$ = 8.0 Hz , $^2J_{PP}$ = 7.7 Hz , P_A) ; δ - 6.3 (dd , $^2J_{PP}$ = 7.7 Hz , $^2J_{PP}$ = 32.3 Hz , P_B) ; δ - 9.8 (dd , $^2J_{PP}$ = 8.0 Hz , $^2J_{PP}$ = 32.3 Hz , P_C). Found : C , 52.3 ; H , 8.0. $C_{21}H_{37}P_3Ru$ requires : C , 52.5 ; H , 7.7.

Trans-chlorohydridotetrakis(methyldiphenylphosphine)rut henium(II)

To a suspension of [$RuHCl(PPh_3)_3$] , (1.0 g , 9.85 x 10^{-3} mol) , in light petroleum ether was added a 6 molar equivalent of PPh_2Me , (1.2 g , 6 x 10^{-3} mol). After stirring for 12 h , the solution was filtered to leave a yellow powder which after recrystallization from diethyl ether gave small yellow crystals identified as the title compound. Yield 0.58 g (63 %). ^1H n.m.r (benzene-d_6 ,300 MHz , 298 k) : δ 7.83 - 6.82 (complex , aromatic) ; δ 2.09 (bs , PMe) ; δ - 17.80 (qu , $^2J_{PH}$ = 20.84 Hz). ^{31}P-{^1H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 20.09 (s).

Trans-chlorohydridotetrakis(dimethylphenylphosphine)rut henium(II)

To a suspension of [$RuHCl(PPh_3)_3$] , (1.0 g , 9.85 x 10^{-3} mol) , in light petroleum ether was added a 6 molar equivalent of PMe2Ph , (0.8 g , 6 x 10^{-3} mol). After stirring for 18 h , the solution was filtered leaving a yellow oil which could not be purified further but which was identified by n.m.r. ^1H n.m.r (benzene-d_6 ,300 MHz ,298 k) : δ 8.05 - 6.94 (complex ,aromatic) ;

δ 1.61 (bs , PMe) ; δ - 18.28 (qu , $^{2}J_{PH}$ = 20.47 Hz). ^{31}P-{^{1}H} n.m.r (benzene-d_6 , 120.81 MHz , 298 K) : δ 8.94 (bs).

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